

Strained Cyclic Cumulenes

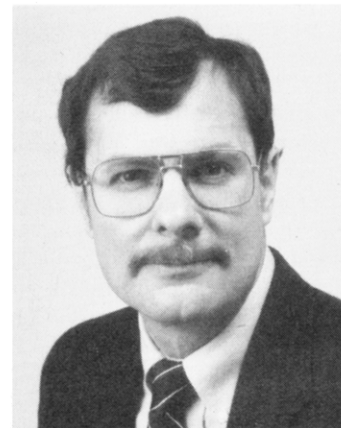
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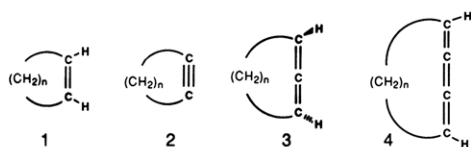
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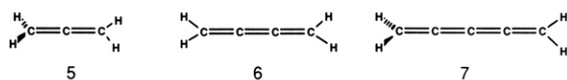
I. Introduction

Structural limitations in hydrocarbons have posed a longstanding challenge to chemists.¹ One highly fundamental question is the incorporation of multiple bonds in small cyclic structures, whose constraints engender substantial strain energy and resultant reactivity. For simple cycloalkenes (1), there is no limiting ring



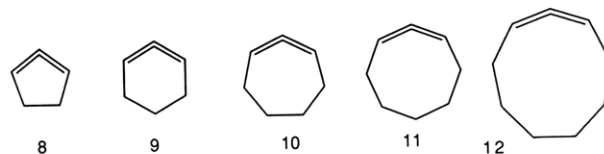
size; cyclopropenes (1, $n = 1$), which have >50 kcal/mol of strain energy, are readily prepared and isolated.¹ Simple cycloalkynes (2) become unisolable for rings with fewer than eight carbons; these are described in a recent review.² Cyclic cumulenes, principally structures such as 3 and 4 are the subject of the present review. One of the most fascinating aspects of these compounds is their smooth transition from shelf-stable substances to reactive intermediates as ring size diminishes.

Cumulenes are the homologous series of hydrocarbons that contain multiple, sequential double bonds sharing common atoms.³ Allene (1,2-propadiene (5)), 1,2,3-butatriene (6), and 1,2,3,4-pentatetraene (7) are the first



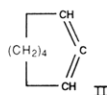
three members of this series. All have linear equilibrium geometries, with the four attached ligands alternating along the series between planar (D_{2h}) and or-

thogonal (D_{2d}) arrangements. Many aspects of cumulene stereochemistry, synthesis, and reactivity have been investigated; some of these are treated in recent reviews.⁴⁻⁸ Linear cumulenes are *not* inherently "strained". Strain implies some deviation from an ideal bonding geometry; this is not true for 5-7, which contain ordinary sp - and sp^2 -hybridized carbons. Nevertheless, the electronic structure of cumulenes and their ability to form stabilized intermediates do render them highly reactive. Unsubstituted higher cumulenes such as 6 and 7 readily polymerize when not in dilute solution. Many allenes dimerize easily. As with cycloalkenes and cycloalkynes, ring constraints in cyclic cumulenes cause increasing angle strain as the ring size diminishes from 12 to 8. At present, fundamental questions of structure, isolability, and chemical reactivity of strained cyclic cumulenes have been only partially answered.⁶



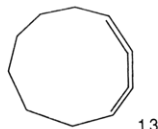
The first reported attempts to synthesize strained cyclic allenes date to the mid-1930s in the laboratory of Favorski in Leningrad. Amazingly, in 1936 Favorski obtained a distillable hydrocarbon by treating 1-

bromo-2-chlorocycloheptene with sodium in ether and reported: "The results obtained show definitively that the hydrocarbon of formula C_7H_{10} contains an allenic group in the ring and corresponds to formula II."⁹ This



was erroneous, but the result remained unchallenged for 25 years! In the 1940s, Domnin, a student of Favorski, reported unsuccessful attempts to isolate 1,2-cyclohexadiene (9).¹⁰ The next pioneering work on strained allenes was carried out during the 1960s by Ball and Landor at Woolrich Polytechnic (London), who appear to be the first to successfully make 1,2-cycloheptadiene (10) and 1,2-cyclooctadiene (11).¹¹ Both of these readily dimerize and were not isolable. Since this time, numerous strained cyclic allenes have been described, either as putative reaction intermediates or isolable substances.

Far less is known about higher cyclic cumulenes. The first known cyclic butatriene was 1,2,3-cyclododecatriene (13), reported in 1967 by Moore and Ozretich.¹² Only



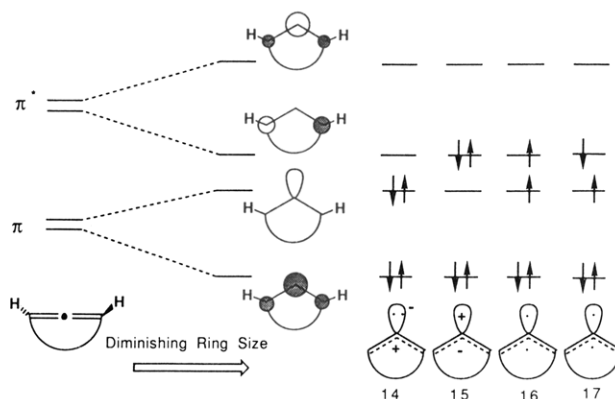
recently have the strained seven-^{13,14} and nine-membered-ring¹⁵ homologues been prepared. There appear to be no examples of strained higher cumulenes, although some unstrained cyclic cumulenes have been prepared.

Various aspects of strained cumulene chemistry have been reviewed in the past.^{1,3-6} The present review is an effort to collect these results in a comprehensive fashion, with a natural organization based on ring size. The synthesis and chemical reactions of strained cumulenes are presented throughout. For completeness, there are included a few examples of cumulene structure types for which only unstrained homologues currently are known.

II. Strained Cyclic Allenes

A. Origins and Estimates of Strain

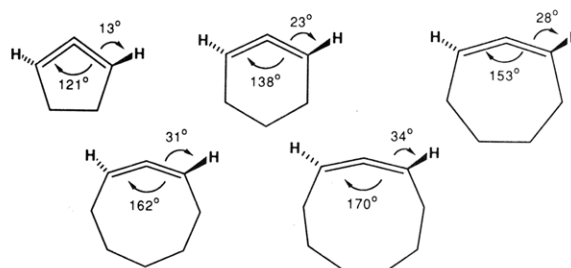
The equilibrium geometry for allene is linear, with orthogonal pairs of substituents. Ring constraints bend the allene and exert torsion toward a planar arrangement of ligands. Model semiempirical¹⁶ and *ab initio*¹⁷ molecular orbital calculations show that the bending potential is remarkably soft for the first 20°, resulting in only ca. 4 kcal/mol estimated strain, but rises steeply beyond this. Moreover, calculations show that bending and torsion are coupled motions; optimized structures for artificially bent allene show the hydrogens twisted toward planarity.^{16,18} In bent allenes, the majority of strain derives from the weakened π bonds. Bending also destroys the degeneracy of π and π^* orbitals; correlation with orbitals of planar allene is shown in the following diagram.¹⁹ The molecular orbitals of planar allene are best described as an allyl system, orthogonal to an sp^2 hybrid orbital.



Molecular models readily demonstrate that rings of ten or more carbons will accommodate an allene without geometric deformation and its concomitant strain. In rings of nine carbons or fewer, there should be increasing strain, as the allene bends. Eventually the allene may be forced to planarity, although it is not yet known for what ring size this occurs. Among the possible electronic configurations for bent planar allene, the order predicted by *ab initio* calculations is $15 > 14 > 16 > 17$ (ground state).¹⁹ The zwitterions 14 and 15 are excited states. Interestingly, *ab initio* MCSCF calculations predict a *singlet* ground state (17) for diradical planar allene with a singlet-triplet gap of 4.9 kcal/mol.

Structural data for strained cyclic allenes are sparse. For 1,2-cyclononadiene (12), electron diffraction studies²⁰ and a crystal structure²¹ for one derivative predict the allene to be bent from linearity by 10°. Force field calculations with several different parametrizations²² and semiempirical MNDO calculations²³ give very similar results. It is also apparent that the hydrogens in 12 are twisted about 20° toward planarity. The preferred conformation has C_1 symmetry.^{20,22}

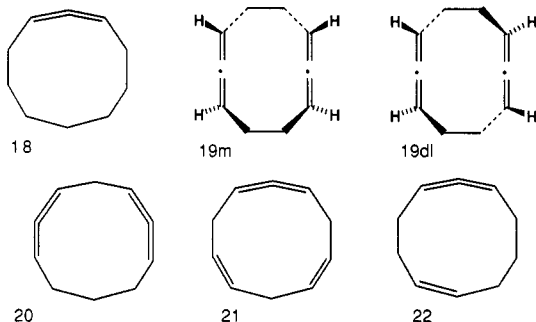
In smaller cyclic allenes, ring constraints must increase bending, torsion, and strain. Predicted bending angles and out-of-plane torsional angles from MNDO calculations^{23a} are summarized below; other approaches yield similar results. Crude strain estimates of 30, 20,



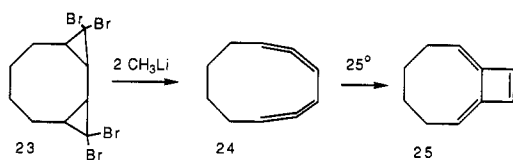
15, and 10 kcal/mol for five- to eight-membered-ring allenes, respectively, were first reported by Gasteiger and Dammer.²⁴ Because bent, planar allene should be *unstrained* by ring constraints,^{23b} the maximum strain that might be accommodated by an allene unit must be ca. 46 kcal/mol, which corresponds to the ground-state rotational barrier. Comparison of this value with *ab initio* predictions for the barrier in 8 and 9 permitted strain estimates of 41 and 31 kcal/mol, respectively.²³ Yavari employed force field methods to estimate 14 kcal/mol of total strain in 11. More accurate estimates of strain energy are needed for these compounds.

B. Ten-Membered-Ring Allenes

While 1,2-cyclodecadiene (18) should suffer no strain due to ring constraints, some of its simple unsaturated derivatives will be highly strained. There are three isomeric ten-membered ring bisallenenes. Allene 19, first

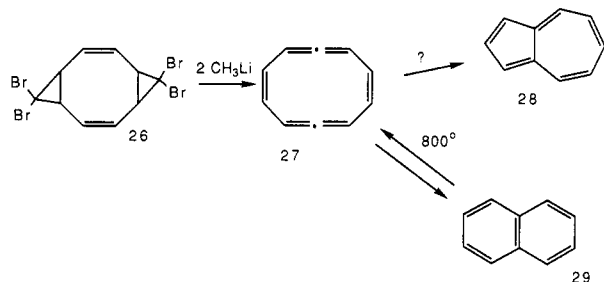


synthesized by Skattebol in 1961, can exist as meso or *dl* stereoisomers—a stereochemical property shared by other bisallenenes. Only the meso structure has been characterized, although the *dl* isomer does not appear to be seriously strained.²⁵ An X-ray structure shows 19m to have allene units bent to 174°, which implies modest strain.²⁶ Conjugated isomer 24 was suggested



by Masamune et al. as an intermediate leading to bicyclic 25.²⁷ Isomer 20, also prepared by the carbenoid route, is less strained (according to models) and proved to be isolable; the authors noted that both diastereomers appear to be formed.²⁸ 1,2-Cyclodecadienes 21 and 22 also have been reported.^{29,30}

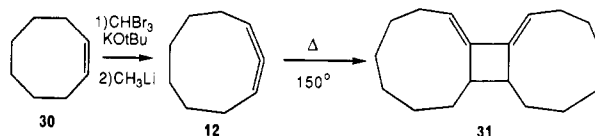
In their classic treatise on orbital symmetry, Woodward and Hoffmann predicted the two isomers of allene 27 to have a "...very fragile grasp on existence", not because of inherent high strain, but rather their expected facile electrocyclization to naphthalene.³¹ A few



years later, this prediction was verified by Dehmlow and Ezimora.³² More recently, allene 27 or a related diradical has been posited by Scott as one intermediate in the remarkable high-temperature rearrangement of naphthalene to azulene.³³ Dewar has reported computations on 27 and reaction paths leading to naphthalene.³⁴

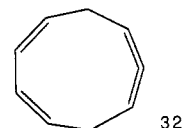
C. Nine-Membered-Ring Allenes

1,2-Cyclononadiene (12), first synthesized in 1951 by Blomquist and co-workers,³⁵ is the best studied cyclic allene. As later shown by Skattebol, this compound

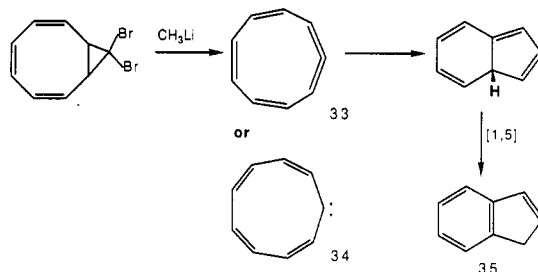


is easily prepared in multigram quantities and >99% purity by ring expansion of cyclooctene.²⁵ Allene 12 dimerizes upon heating. This general two-step approach continues to be widely applied to cyclic allene synthesis.⁴ Allene 12 is bent to 170°, which indicates a strain energy of <5 kcal/mol.

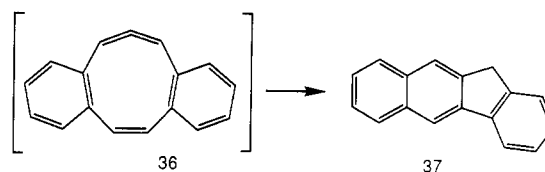
Unsaturated derivatives of 12 are more reactive. In 1976, Baird and Reese reported that allene 32 dimerizes with a half-life of ca. 10 min at 0 °C.²⁸ Enhanced



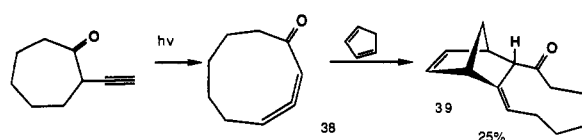
reactivity of 32 is probably due to increased ring strain caused by the additional double bonds. Waali and Allison have reported that the highly unsaturated allene 33 may be prepared by the classic carbenoid route.



This compound could not be isolated; its intermediacy was inferred from a 36% yield of indene (35).³⁶ Similar preparation of a dibenzo derivative yielded 37. The

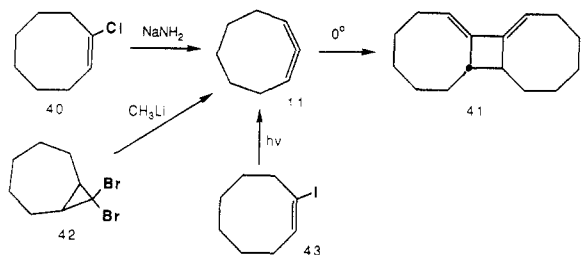


authors noted that electrocyclization of 33 and 36 should be favored by geometric proximity of C₂ and C₆. Although trapping experiments might inspire more confidence in the intermediacy of allene 33, there seems no reason to doubt the present conclusions. Semi-empirical MO calculations by the same authors show a chiral C₂ structure for 33 and suggest that the isomeric carbene 34 is not an energy minimum.³⁷ One other interesting nine-membered-ring allene is allenone 38, which may be prepared either by the carbenoid route or by photochemical ring expansion.³⁸



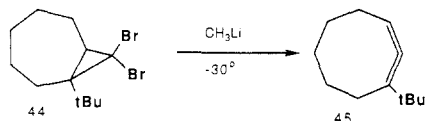
D. Eight-Membered-Ring Allenes

The synthesis of 1,2-cyclooctadiene (11) was first reported by Ball and Landor in 1961.¹¹ Dehydrohalogenation of 1-chlorocyclooctene (40) afforded tricyclic



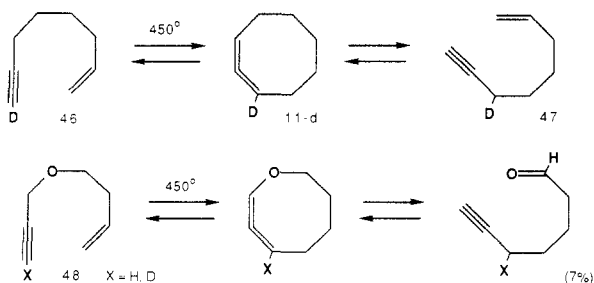
diene **41**, presumed to be the allene dimer. The facile dimerization of strained allenes such as **11** doubtless results from twofold strain release upon C₂-C₂ bonding. Wittig employed the same reaction several years later and also succeeded in trapping **11** with diphenylisobenzofuran.³⁹ Marquis and Gardner were the first to report the carbenoid route (via **42**), which probably is the best preparation of **11**.⁴⁰ This strained allene readily dimerizes, but cold, dilute solutions are suitable for rapid NMR and IR analysis.⁴¹ The IR stretching frequency is 1950 cm⁻¹, only slightly reduced from 1956 cm⁻¹ in **12**.⁴² Semiempirical MO calculations support the expectation that allene vibrational frequencies should decrease with bending.⁴² We have also found it feasible to add dibromocarbene to **11** at low temperature.¹⁵ MNDO²³ and force field calculations predict the allene unit to be bent by ca. 20°.

The 1-methyl derivative of **11** enjoys greater kinetic stability and dimerizes with a half-life of 10–15 min at ambient temperature.⁴² To date, the only isolable 1,2-cyclooctadiene is the 1-*tert*-butyl derivative **45**,



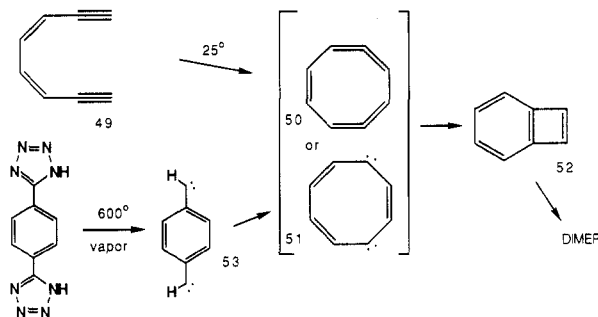
which we reported in 1986.⁴³ This was prepared in modest yield by the carbenoid route and was found to be sufficiently stable for purification by preparative GLC. Characterization as an allene followed from IR (1942 cm⁻¹) and ¹³C NMR (resonances at 202.2, 117.7, and 94.4 ppm) data. Facile acid- or base-catalyzed rearrangements to conjugated dienes were observed.

Several more novel approaches to **11** have been reported. Kropp suggested **11** as an intermediate in photolysis of vinyl iodide **43** in methanol.⁴⁴ The allene is assumed to be easily protonated under the reaction conditions, and ethers are the major products. Shea and co-workers recently reported evidence that 1,2-cyclooctadiene is an intermediate in flash thermolysis of enyne **46**.⁴⁵ Intramolecular "ene" reaction results

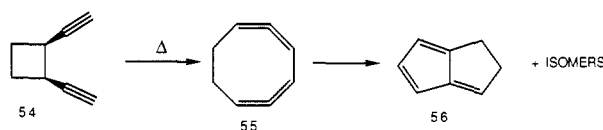


in a degenerate process that rapidly scrambles the deuterium label. The reverse process had been observed in thermolysis of 1,2-cyclononadiene.⁴⁶ This novel approach was also applied to the nondegenerate rearrangement of ether **48**, albeit in low yield.⁴⁵

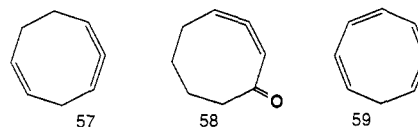
Quite a variety of more complex 1,2-cyclooctadienes have been postulated as reaction intermediates. Classic examples are the electrocyclization of **49**, reported by



Mitchell and Sondheimer,⁴⁷ and Cope rearrangement of **54**, described by Eisenhuth and Hopf.⁴⁸ Recently,

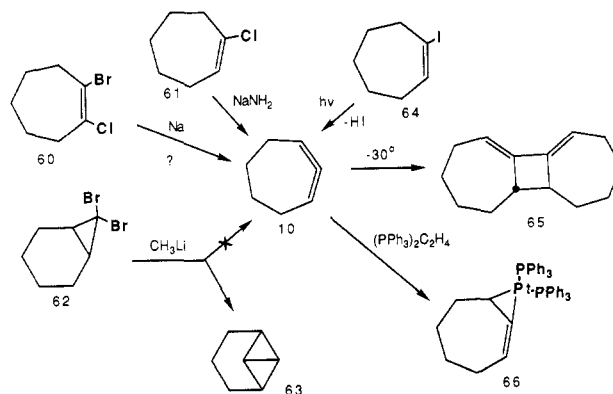


Wentrup has also suggested bisallene **50** as an intermediate in the rearrangement of biscarbene **53** to benzocyclobutadiene (**52**).⁴⁹ Other reported examples of eight-membered-ring allenes include **57**,⁵⁰ **58**,⁵¹ and **59**,⁵² none of which proved isolable.



E. Seven-Membered-Ring Allenes

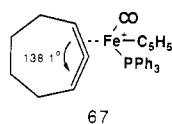
As noted in the Introduction, Favorski and co-workers believed they had synthesized 1,2-cycloheptadiene (**10**) around 1936 by treatment of **60** with sodium.⁹



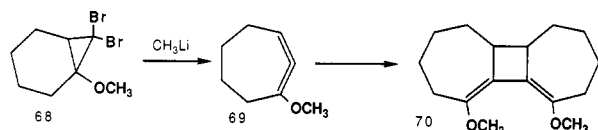
This result remained unchallenged until 1961, when Ball and Landor employed the dehydrohalogenation route and isolated the [2 + 2] dimer **65**.¹¹ To date, allene **10** has proved too reactive to be isolated or even to be observed spectroscopically.^{53,54} On the basis of the behavior of **45**, we speculate that *tert*-butyl-1,2-cycloheptadiene might be isolable. MNDO calculations on **10** predict a structure with an allene bending angle of 153° and the two hydrogens twisted 28° out of plane. Evidence for the chirality of **10** was provided by Balci and Jones, who isolated optically active cycloadducts by two different routes.⁵⁵ The allene has also been trapped by diphenylisobenzofuran and by formation of

platinum and iron complexes.^{54,56} Ligand displacement from **66** at $-25\text{ }^{\circ}\text{C}$ with CS_2 yielded only dimer; by contrast, the eight-membered-ring allene **11** could be observed under these conditions.⁵⁴ One other approach to **10** has been photolysis of vinyl iodide **64**, a reaction reported recently by Kropp.⁴⁴

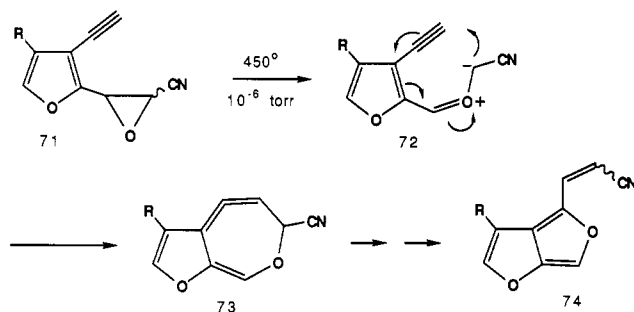
Jones and co-workers have recently reported the first crystal structure for a 1,2-cycloheptadiene-iron complex (**67**). This complex shows an allene unit that is bent slightly more than in the predicted structure of **10**.⁵⁶



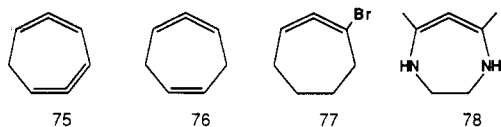
Somewhat paradoxically, the carbenoid route to **10** is not successful; C-H insertion yields largely strained bicyclobutane **63**. It is interesting that this route *does* succeed for the methoxy derivative **69**; dimer **70** was isolated in 85% yield.⁵⁷



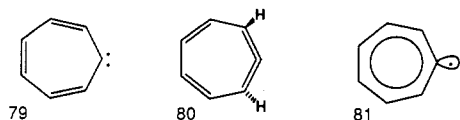
Quite a number of 1,2-cycloheptadiene derivatives have been postulated as reactive intermediates. Among recent examples, Eberbach and co-workers have reported a general approach based on intramolecular reaction of oxygen ylides.⁵⁹ A recent example is found



in the flash thermolysis of **71**, which presumably generates allene **73**. Other cases of seven-membered-ring allene intermediates include **75-78**.^{53,58,60,61}



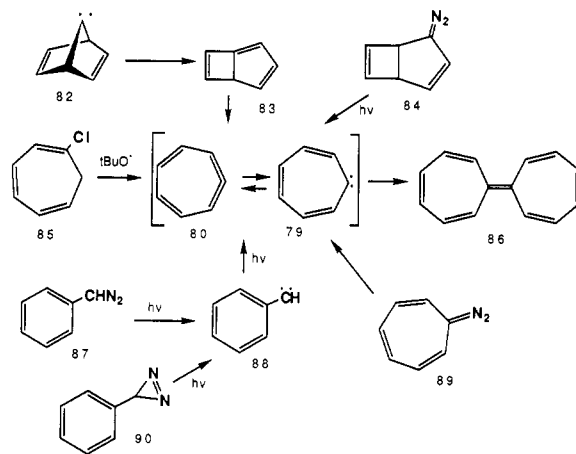
The C_7H_6 potential energy surface has been the focus of enormous attention during the past several decades.⁶²⁻⁶⁹ Among well-known C_7H_6 isomers are cycloheptatrienyliene (**79**) and 1,2,4,6-cycloheptatetraene



(**80**). Strained allene **80** plays a central role in C_7H_6 interconversions; indeed, for this reason it may be the best studied strained cyclic cumulene. Major questions have included the allenic character of this reactive species, its chirality, and potential interconversion with

carbene **79**. This work has been reviewed at various stages.⁶³ As noted in 1987 by Chapman, "...current wisdom holds that singlet cycloheptatrienyliene is a discrete intermediate and that it thermally equilibrates with cycloheptatetraene".⁶²

There exist numerous routes for preparing these intermediates. These include low-temperature matrix photolysis of phenylmethylene (**88**) and a number of high-temperature pyrolytic methods. In the absence of other trapping agents, heptafulvalene (**86**) is the observed product. In principle, this could result from dimerization of either **79** or **80**.

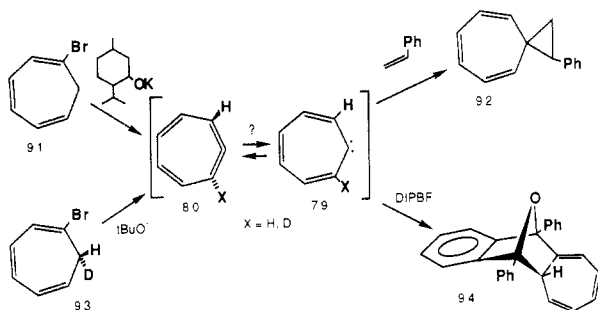


Compelling evidence in favor of an allenic structure derives from three sources. First, semiempirical and ab initio molecular orbital calculations clearly show a minimum for a chiral allenic geometry, i.e., a structure with C_2 symmetry.⁶⁹ All calculations reported to date show the strongly bent (ca. 149°) chiral allene to lie 16-48 kcal/mol below the singlet carbene.⁶⁹ These calculations probably overestimate the magnitude of this gap. A further complication is the uncertain energetics of the triplet carbene, best described as **81**. Waali employed MNDO calculations to predict that singlet carbene **79** should be a transition state, rather than an energy minimum.^{69d} More recently, Janssen and Schaefer reported calculations at the DZ TCSCF (two-configuration SCF) level that show, probably reliably, that singlet carbene **79** is a bona fide energy minimum, although the energy relative to **80** was not predicted.^{69e} Somewhat problematic have been two independent reports by Chapman⁶⁸ and Wentrup⁶⁷ of a triplet ESR signal for photogenerated cycloheptatrienyliene. Unfortunately, the two papers reported different D values for the triplet, which suggests that one is in error. In both cases, warming the matrix slightly led to irreversible loss of the ESR signal; Wentrup interpreted this result as conversion to singlet **80**. To confuse this issue further, the energetics of the open-shell singlet state of cycloheptatrienyliene (**81**) are uncertain. We speculate that this will be nearly isoenergetic with the closed-shell singlet, an argument supported by recent calculations on lower homologue cyclopentadienyliene.⁷⁰ Whatever the carbene energetics, it is probably true that allene **80** is the lowest energy species here, with the carbene a shallow energy minimum.

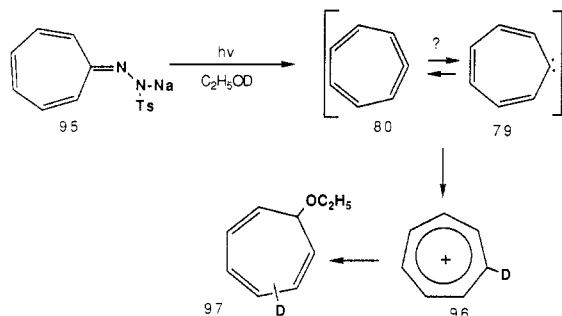
Chapman has reported IR and UV spectra for matrix-isolated **80**, which was generated from a variety of precursors.⁶² IR bands at 1824 and 1816 cm^{-1} were

assigned to allene stretching vibrations. It is unclear why two bands are observed. Data for 1-deuterio, fluoro, and chloro derivatives also were reported. The UV spectrum of allene **80** did not show a defined maximum above 200 nm, which seems surprising for a structure with this degree of conjugation.

Evidence that **80** possesses a chiral equilibrium geometry derives from clever experiments by Harris and Jones.⁶⁵ Their approach was to generate and trap *optically active* cycloheptatetraene, based on reasoning that the planar carbene would be *achiral*. Two approaches were employed, the first with a chiral base, potassium menthoxide, and bromide **91**, and the second with an achiral base and chiral deuterated precursor (**93**). Both experiments yielded optically active adducts



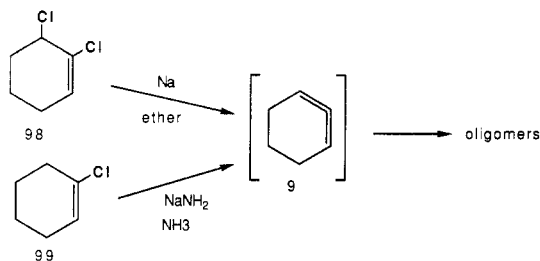
with diphenylisobenzofuran (DIBF), which led Jones to conclude that the allene must be chiral. However, in the presence of styrene, optically *inactive* spiro adduct **92** was isolated; this was attributed to stepwise addition or an achiral carbene progenitor. Kirmse also provided evidence for a carbene by trapping experiments with alcohol. Irradiation of tosylhydrazone **95** in C_2H_5OD yielded ether **97**, with a statistical deuterium distribution.⁶⁴ This was attributed to reaction of a carbene, rather than a cyclic allene.



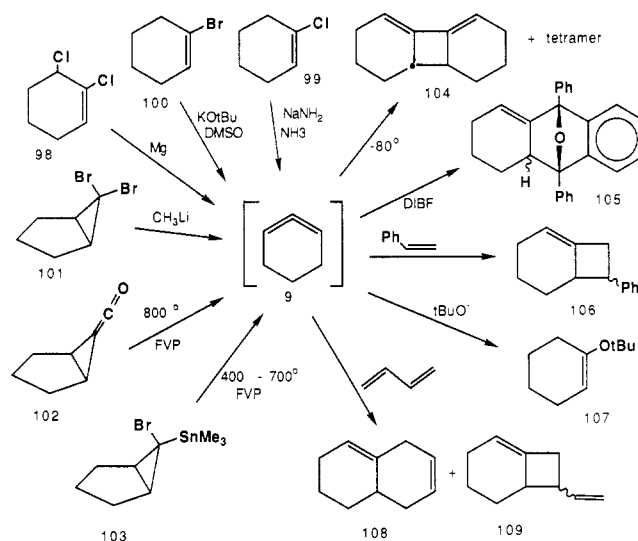
The most economical interpretation of these results is that the planar carbene and chiral allene both exist and are separated by a modest barrier, but one small enough to "merge" their chemical behavior. The role of the open-shell (singlet or triplet **81**) carbene remains unclear.

F. Six-Membered-Ring Allenes

There is a surprising amount of early literature on 1,2-cyclohexadienes. Early attempts to synthesize and isolate 1,2-cyclohexadiene (**9**) and its strained isomer cyclohexyne were made around 1935 in the laboratory of Favorski.⁹ The first reported synthesis which may have succeeded was due to Domnin, a co-worker of Favorski.¹⁰ Treatment of dichlorocyclohexene (**98**) with sodium in ether yielded $(C_6H_8)_n$ oligomers, including a "distillable tetramer". Twenty years later, Ball and

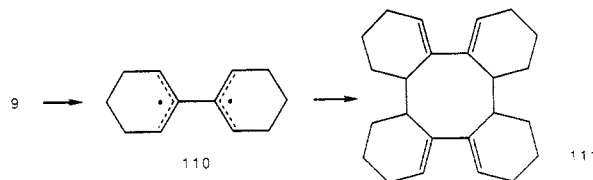


Landor reported isolation of similar nonvolatile oligomers upon dehydrohalogenation of 1-chlorocyclohexene (**99**).¹¹ Presumably, both of these reactions generate transient **9**. The first clear demonstration of the existence of 1,2-cyclohexadiene was reported by Wittig and Fritze in 1966.⁷¹ Reaction of 1-bromocyclohexene (**100**) with *t*-BuOK/DMSO yielded [2 + 2]



dimer **104** (ca. 7%). Additionally, trapping of **9** with diphenylisobenzofuran afforded two stereoisomeric cycloadducts (**105**). Subsequent labeling studies by Bottini provided evidence against cyclohexyne intermediates in these reactions.⁷²

Known routes to **9** are summarized in the scheme above.⁷¹⁻⁸⁰ The most efficient method is by reaction of 6,6-dibromobicyclo[3.1.0]hexane (**101**) with methyl-lithium, a reaction first reported by Moore and Moser.⁷³ Trapping by [2 + 2] cycloaddition with styrene was observed. In a subsequent paper, the same authors reported that at $-80^\circ C$, allene **9** yields mostly (61%) two stereoisomeric tetramers (**111**), probably formed by dimerization of bisallyl intermediate **110**. At $35^\circ C$, the major product was crystalline dimer **104** (55% yield).



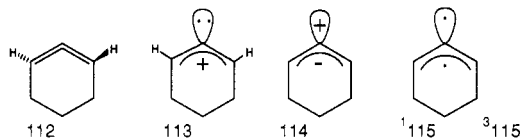
Other comprehensive studies are due to Bottini, who trapped **9** with conjugated dienes, styrene, furan, and nucleophilic addition of *tert*-butoxide.⁷⁴ More recently, Christl and Schreck have reported careful studies of reactions with acyclic 1,3-dienes.^{78,79} The dominant reaction mode is [2 + 2] cycloaddition (to **109**), but some [2 + 4] adduct is observed with 1,3-butadiene. 1-Methyl-1,2-cyclohexadiene has been studied by the

same authors. Waali has studied reactions of **9** with deuterium-labeled styrene and concluded that addition to form **106** is stepwise.⁸⁰

There are two recent reports that **9** may be observed in a cryogenic matrix. Wentrup pyrolyzed ketene **102** and trapped an intermediate that displayed an IR absorption at 1886 cm^{-1} .⁷⁶ Dimer **104** was formed upon warming the matrix. More recently, Runge and Sander reported that pyrolysis of **103** at 500 °C yields an intermediate with infrared absorption at 1829 cm^{-1} .⁷⁷ At higher temperatures, retrograde [2 + 4] fragmentation to vinylacetylene and ethylene was observed. As described below, the reverse cycloaddition process may also occur in some cases.

The discrepancy between these two observed IR stretching frequencies suggests that one of these studies may be in error. Semiempirical MNDO calculations, with calibration by experimental data for known cyclic cumulenes, predict a vibrational frequency of 1850 cm^{-1} for **9**.⁸¹

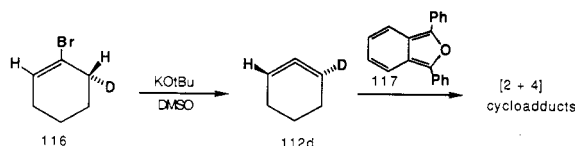
The structure of 1,2-cyclohexadiene has proved problematic, in part because of some mistaken ideas about the structure of planar allene. One potential structure is a chiral (C_2) molecule (**112**) in which the two π bonds



are intact, but badly distorted. Alternatively, ring constraints might enforce planarity at C_1 - C_3 , leaving an allyl fragment orthogonal to a nonbonding sp^2 hybrid orbital. As described above, this species might correspond to a singlet or triplet diradical (**115**) or two possible zwitterions (**113**, **114**).

Ball and Landor originally suggested "... sp^2 hybridization for carbon atoms 1, 2, and 3 with an unbonded electron on carbon atom 2".¹¹ Moore and Moser later predicted that either zwitterion **113** or the triplet diradical ³**115** could be the ground state of **9**. Either formulation seemed consistent with the observed high reactivity. Zwitterion **113** found further support in model INDO calculations on allene, reported by Dillon and Underwood.⁸² Unfortunately, these calculations were for the wrong electronic state, i.e., 14 rather than 17. Bottini and co-workers felt their experimental studies on **9** were consistent with *both* zwitterion and singlet diradical species.⁷⁴

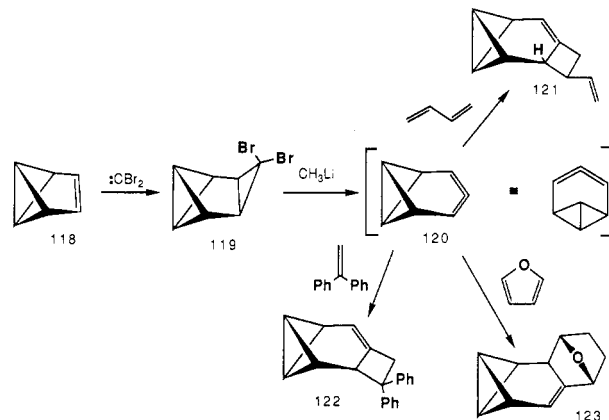
Current evidence points clearly toward a chiral allenic structure, with singlet diradical **115** a transition state for enantiomeric interconversion. The chirality of **9** was demonstrated by Balci and Jones, who prepared optically active **9** from a monodeuterated precursor (**116**, absolute configuration unknown) and trapped it to give active cycloadducts.⁷⁵ This result relies on an expected isotope effect and concerted dehydrohalogenation.



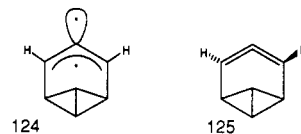
Ab initio calculations also support the chiral allenic structure. Geometry optimization (HF/STO-3G) showed an energy minimum for the chiral structure **112**,

which, at the 20-configuration MCSCF or MP2 level was 15–25 kcal/mol below diradical ¹**115**.²³ In this structure, the allene structural unit is bent to 135° and the two allenic hydrogens are bent in opposite directions 30.4° out of plane. The observed IR stretch at ca. 1850 cm^{-1} (see above) is consistent with an intact allene unit and is well modeled by semiempirical MO calculations.⁸¹

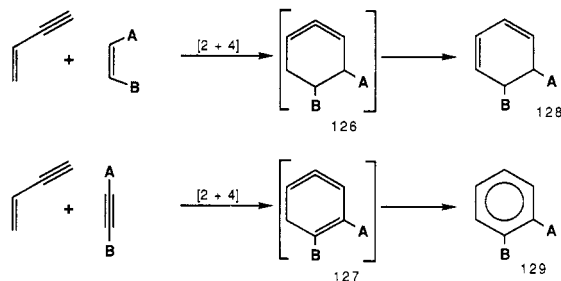
Christl and co-workers have reported a thorough investigation of the unusual hydrocarbon **120**, which is



prepared from benzvalene (**118**) and incorporates two highly strained functionalities.⁸³ Although dimers could not be isolated, allene **120** was successfully trapped by styrene, 1,1-diphenylethylene, furan, and various 1,3-dienes. On the basis of the severe ring constraints and observed reactions of **120**, Christl concluded that the best description was as diradical **124**. A more likely structure may be the chiral allene **125**, although this is probably only a few kcal/mol lower.

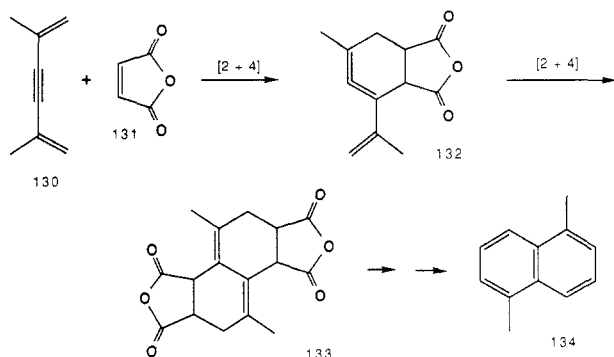


1,2-Cyclohexadienes of types **126** and **127** may be intermediates in the "dehydro" Diels–Alder reaction, a general cycloaddition in which a vinylacetylene serves as the 1,3-diene.^{84–86} The mechanism of this interesting

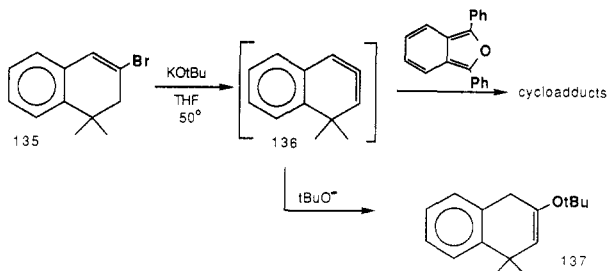


and long-known cycloaddition remains poorly understood; some cases may be acid catalyzed,⁸⁶ but others might involve strained allenes. In one early example, Butz and co-workers studied the double cycloaddition of maleic anhydride to dienyne **130** and appear to be the first to have suggested an intermediate 1,2-cyclohexadiene.⁸⁵ Other cases with alkyne dienophiles may involve 1,2,4-cyclohexatrienes.⁸⁴ In view of the ready formation of 1,2-cyclohexadienes from numerous sources, the mechanism of the dehydro Diels–Alder reaction bears closer scrutiny.

The first clear example of a 1,2,4-cyclohexatriene was recently reported by Miller and Shi, who described this

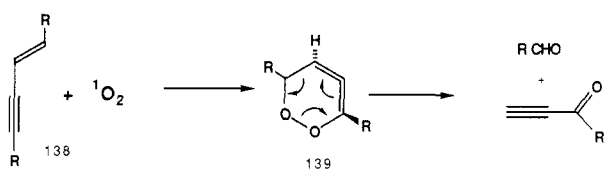


as an "isoaromatic" molecule.⁸⁷ Dehydrobromination of 135 in the presence of diphenylisobenzofuran af-

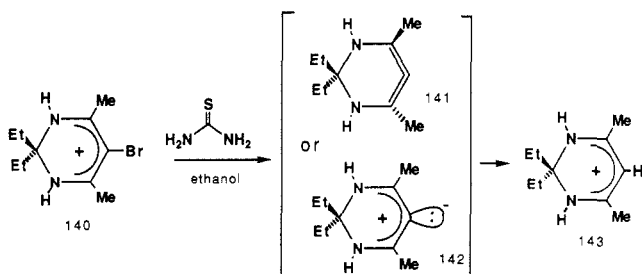


forded two cycloadducts, which appear to result from allene 136. Once again, this structure may exist as a chiral allene, separated by only a few kcal/mol from a planar diradical.

Heterocyclic derivatives of 1,2-cyclohexadiene also have been described. Lee-Ruff and co-workers reported that addition of singlet oxygen to conjugated enynes (138) afforded fragmentation products, which support an intermediate allene.⁸⁸



Ab initio geometry optimization for 139 (R = H) yielded a chiral structure, with a predicted inversion barrier of 28 kcal/mol. Lloyd and co-workers have studied protodebromination of cation 140 and inferred the intermediacy of allene 141.⁵⁸ MNDO calculations

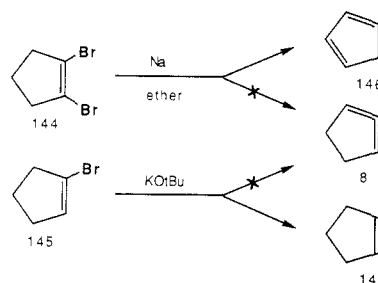


on 141 also were reported to show a strongly bent chiral allene. Resonance-stabilized zwitterion 142 was predicted to be of higher energy. In this case, experimental evidence for the allene intermediate is inconclusive.

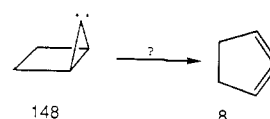
G. Five-Membered-Ring Allenes

Experimental evidence for 1,2-cyclopentadiene has remained elusive. Around 1935, Favorski first attempted to prepare this highly strained allene by

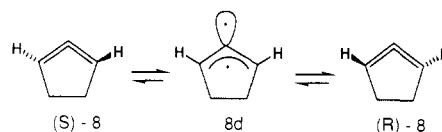
treatment of dibromide 144 with metallic sodium,⁹ a



technique that does succeed for larger ring allenenes. The product was 1,3-cyclopentadiene. Subsequent dehydrohalogenation experiments with vinyl bromide 145 yielded evidence for cyclopentyne (147) rather than allene 8.⁸⁹ In principle, the best route to 1,2-cyclopentadiene should be through cyclopropylidene 148, a route yet to be reported.

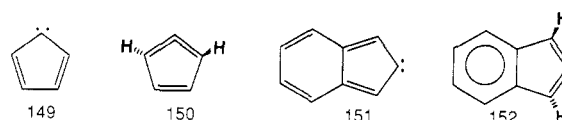


Ab initio calculations on 8 unexpectedly predicted a chiral equilibrium geometry, with the two hydrogens bent 21° out of plane. The inversion barrier (i.e., (S)-8 → 8d → (R)-8) was quite dependent on the method of



calculation, but the highest level used (20-configuration MCSCF) suggested that the chiral structure was lower by 4.9 kcal/mol.²³ This value is well within the anticipated accuracy of the method used.

Cyclopentatriene (150) and cyclopentadienylidene (149) pose a question similar to that described above for their seven- and nine-membered-ring homologues 80 and 33. In the latter cases, the allenic structure

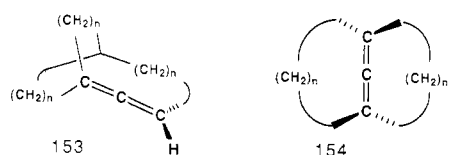


clearly is an energy minimum. For C₅H₄, increased strain may preclude this possibility. Remarkably, MNDO calculations do show an energy minimum for allene 150 (*H_f* = 144.7 kcal/mol), but this is 21.2 kcal/mol above the triplet.³⁷ More recent ab initio (HF/3-21G) calculations for 150 do not predict an energy minimum.⁷⁰ An allenic structure (152) has also been considered by Tolbert for indenylidene (151).⁹⁰ However, the behavior of this species seemed more consistent with an electrophilic carbene. These results seem inconclusive. While these species are almost surely ground-state triplets, we speculate that the *singlet* carbene and allenic structures may be close in energy.

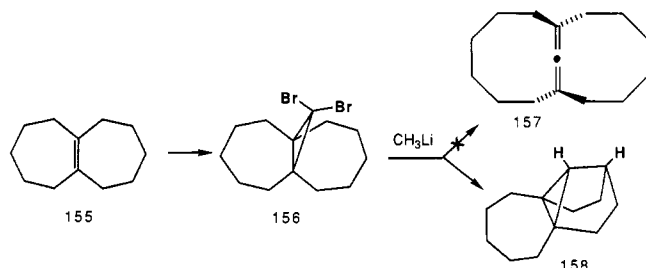
H. Bicyclic Allenes

Although a vast number of bicyclic alkenes are known, the collection of bicyclic cumulenes is remarkably limited. Many fundamental structure types, such

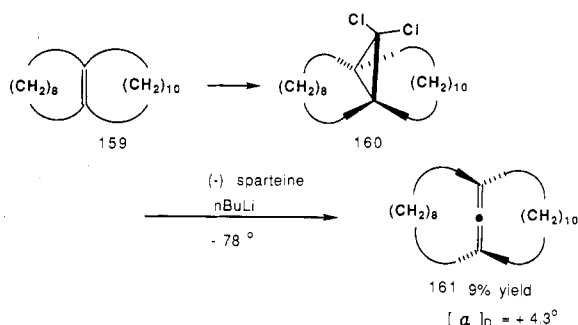
as bridgehead allenes (**153**) remain unknown but should



be amenable to synthesis. The first doubly bridged allene (**154**) was reported in 1982 by Nakazaki and co-workers.⁹¹ Nakazaki reasoned that the limiting structure must have two eight-membered rings, and he attempted to prepare **157** by the carbenoid route. How-

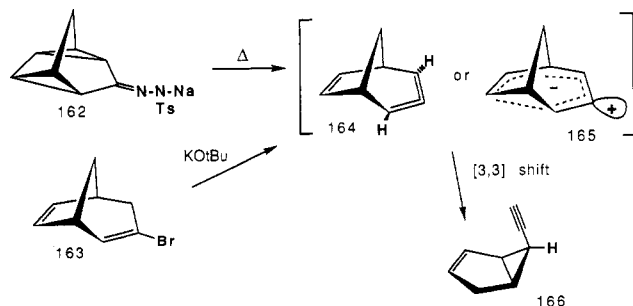


ever, instead of the desired allene, transannular hydrogen insertion, a well-known reaction of carbenoids, yielded **158**. Ring expansion to **160** circumvented this problem and permitted synthesis of unstrained doubly bridged allene **161** in 11% yield among a complex

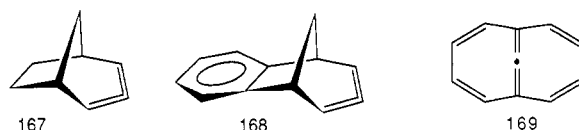


product mixture. Optically active allene **161** was prepared by the use of a sparteine–butyllithium complex. Preparation of smaller homologues such as **157** probably is feasible—it is possible to construct a Dreiding model for **157**—but will require a very different synthetic approach.

There are three examples of bicyclo[3.2.1]octa-2,3-dienes.^{92–94} In 1970, Bergman reported⁹² several routes to strained allene **164**, for which he proposed homo-



aromatic zwitterionic structure **165**. This compound undergoes facile [3,3] sigmatropic rearrangement to alkyne **166**. Other approaches to the same compound, as indicated by formation of **166**, have been reported by Klumpp^{93a} and Freeman.^{93b} Bottini has reported some evidence for the dihydro analogue **167**.⁹⁵ More



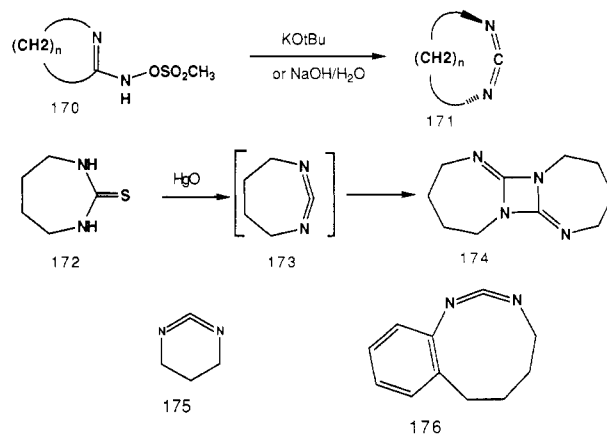
recently, Balci and Harmandar have reported that 6,7-benzo analogue **168** may be trapped by reaction with diphenylisobenzofuran or *tert*-butoxide.⁹⁶ Carlton has offered evidence^{97a} for **169**, but this conclusion was later refuted by Warner.^{97b}

The chirality of allene **164** was demonstrated by Balci and Jones, who employed the same method they used for **9** and **80**.⁹⁴ Dehydrohalogenation of vinyl bromide **163** with potassium methoxide afforded optically active cycloadducts and active alkyne **166**. The optical activity decreased with increasing reaction temperature, which suggests facile racemization. Subsequent MNDO calculations on **164** showed a strongly bent, chiral structure, although the racemization barrier was not accurately estimated.²³

I. Strained Heterocumulenes

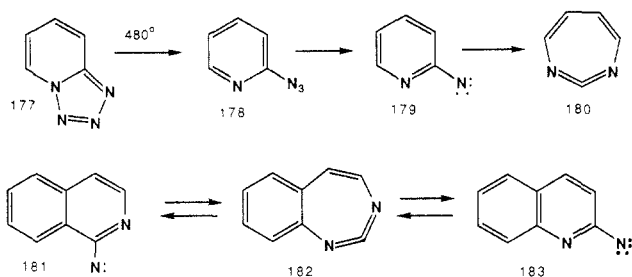
Heterocumulenes are those substances in which one or more carbon atoms of the cumulene are substituted by a heteroatom. An enormous variety of heterocumulenes are known, but only a few have been incorporated in strained rings. There are no quantitative estimates of strain or predicted structures. Some heterocumulenes, such as carbodiimides or isocyanates, are inherently bent. In general, their weaker π bonds present a much softer bending potential than for carbon analogues.

Carbodiimides are the best known among strained heterocumulenes. Richter and co-workers have described a systematic study of the limiting ring size for simple cyclic carbodiimides.⁹⁸ These may be prepared in good yield by the ring-expansion method shown below. Benzo-fused derivative **176** also was prepared.

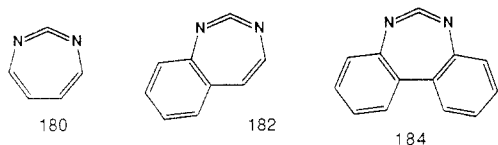


1,3-Diazacycloocta-1,2-diene (**171**, $n = 5$) proved to be the smallest isolable structure; this compound easily oligomerized and was undistillable. Attempts to synthesize the next lower homologue **173** by another method afforded only a [2 + 2] dimer and a possible trimer. Attempts to prepare and trap **175** were unsuccessful.

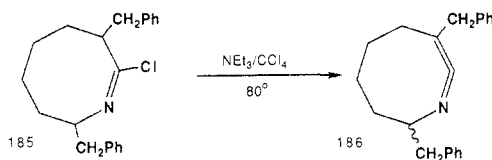
Wentrup and co-workers have reported experimental evidence for a variety of diazacycloheptatetraenes, which are formed by rearrangements of singlet nitrenes.⁹⁹ These reactions are analogous to those described earlier for **80**. Flash vacuum pyrolysis of **177**



at 480 °C with subsequent trapping at -196 °C afforded a reactive substance characterized as carbodiimide **180** by its intense IR absorption at 1975 cm^{-1} . Benzenelated derivatives **182** and **184** were prepared and studied in similar fashion; **184** was stable in the matrix to ca. -40 °C, where it rapidly dimerized.

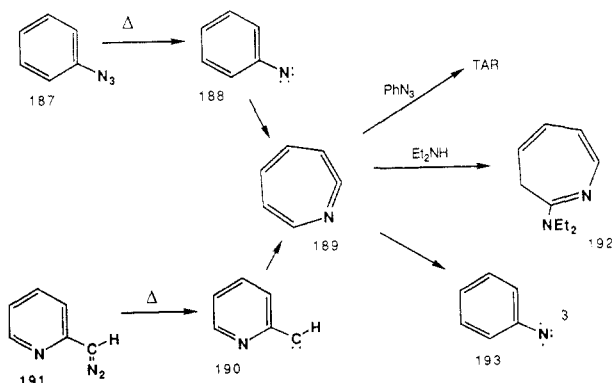


In 1981, Firl and co-workers reported the synthesis of strained ketenimine **186** as a mixture of diastereomers.¹⁰⁰ An observed barrier to diastereomeric inter-



conversion of 19 kcal/mol, 5 kcal/mol greater than for comparable acyclic structures, was attributed to the effects of ring constraints on the transition state.

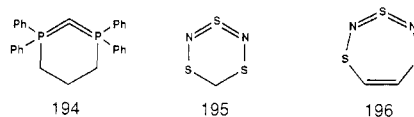
Ketenimine **189**, a didehydroazepine, is a well-known intermediate, with both carbene and nitrene precursors. This strained cumulene plays a key role in the well-studied solution-phase reactions of phenyl azide and phenylnitrene. Chapman^{101a} and Dunkin^{101b} have generated **189** in a cryogenic matrix and assigned the cu-



mulene structure by the intense IR absorption at 1890 cm^{-1} . Recently, Schuster has described solution-phase time-resolved studies on **189**.¹⁰² Transient infrared absorption at 1890 cm^{-1} was observed upon pulsed excimer laser irradiation of dilute solutions of phenyl azide. A lifetime of 4.8 ms was determined. Transient ultraviolet spectra showed that **189** has an absorption maximum at 340 nm. Among the observed reactions of **189** were trapping by amines, reaction with phenyl azide (which presumably results in "tar" formation), and conversion to *triplet* phenylnitrene by spin inversion

and rearrangement. Schuster examined a large collection of substituted phenyl azides and observed dramatic substituent effects on rates for spin inversion and amine addition.

Several other small-ring heterocumulenes have been prepared. Carbodiphosphorane **194** was isolated as a

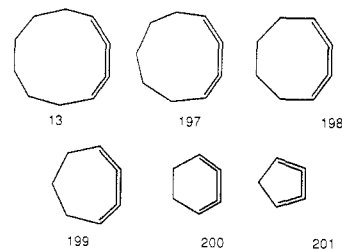


crystalline substance; X-ray crystallography showed a $\text{P}=\text{C}=\text{P}$ angle of 117°.¹⁰³ Trithiadiazine **195** was recently described as a red crystalline substance ($\text{N}=\text{S}=\text{N}$ angle = 120.8°) that results from reaction of diazomethane and S_4N_4 .¹⁰⁴ Cumulene **196** also has been reported.¹⁰⁵ This list is not exhaustive, but it does demonstrate the inherent flexibility of many heterocumulenes.

III. Strained Cyclic Butatrienes

A. Origins and Estimates of Strain

1,2,3-Butatriene (**6**), the next homologous cumulene, exists as a linear, planar structure. The two central carbons are best represented as sp hybridized. Ring constraints introduce primarily in-plane bending, and most of the strain should arise from rehybridization at the central carbons. This will weaken and introduce diradical character in the in-plane π bond, just as pyramidalization affects simple alkenes. Molecular models easily demonstrate that the smallest unstrained (i.e., linear) butatriene would be 1,2,3-cyclodecatriene (**13**). Smaller homologues **197–201** will contain more progressively bent butatriene units, with increasing strain and attendant reactivity.

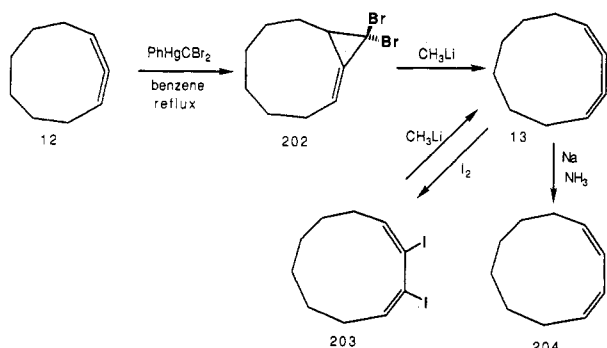


The only quantitative estimates of strain energies and geometries in this series are due to a series of MNDO calculations by our own group.¹⁵ Optimized geometries show the anticipated strong bending, with predicted $\text{C}_1\text{-C}_2\text{-C}_3$ angles of 162–165, 156, 145, 132, and 116° for **197–201**, respectively. Simultaneously the $\text{C}_2\text{-C}_3$ bond is predicted to lengthen as bending occurs; this is consistent with hybridization changes from sp toward sp^2 . Strain was estimated by comparison to model calculations on planar bent butatriene; predicted values were 5.5–8, 14, 31.5, 60.5, and 130 kcal/mol for **197–201**, respectively. These are certainly underestimates for *total* strain, but the data suggest that strain in the butatriene approximately doubles with each decreasing carbon in the ring.

B. Ten- to Five-Membered Rings

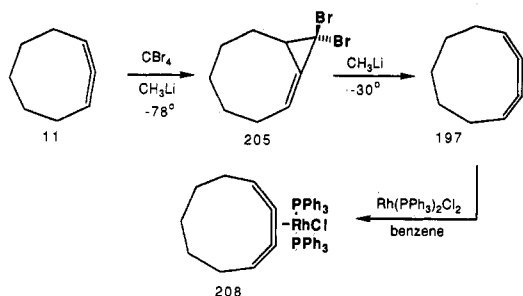
The first known cyclic butatriene was 1,2,3-cyclodecatriene (**13**) reported in 1967 by Moore and Ozre-

tich.¹² Although minimally strained, this compound shares the reactivity of most butatrienes and readily polymerizes upon exposure to oxygen or concentration of solutions. The synthesis of **13** via **202** follows the



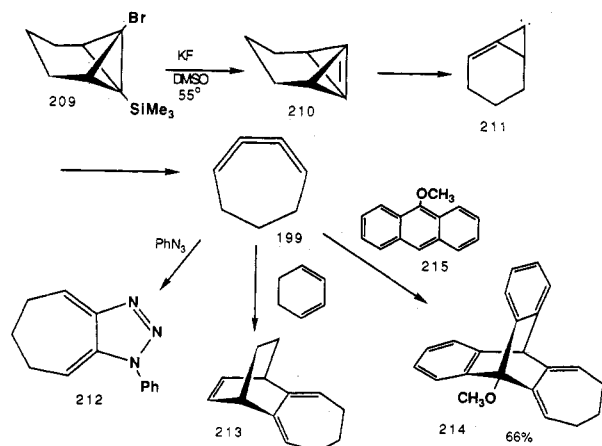
well-known carbenoid route, used extensively for making allenes. A few reactions of cyclic cumulene **13** were studied.¹² Addition of I_2 yielded 2,3-diiodo diene **203**, while dissolving-metal reduction afforded predominantly diene **204**. We have found that direct or triplet-sensitized irradiation of **13** yields mostly polymeric material.¹⁰⁶

The next lower homologue, 1,2,3-cyclononatriene (**197**) was synthesized in 1984 by our own group.¹⁵ A



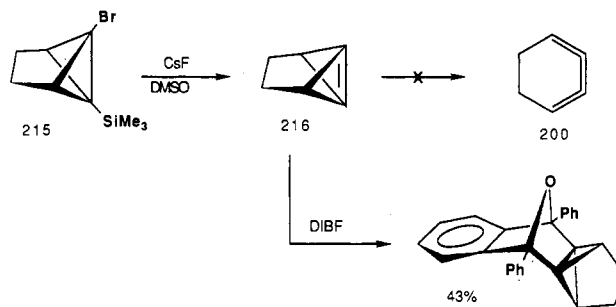
predicted increase in butatriene bending to 165° was consistent with observation of a slight bathochromic shift in the UV spectrum of **197** (λ_{\max} 292 nm) relative to **13** (286 nm). The synthesis of **197** was motivated entirely by our prediction from MNDO calculations that it should not be severely strained. Key to this synthesis was the generation of unstable 1,2-cyclooctadiene (**11**) at -30°C and subsequent reaction with $:CBr_2$ at -78°C . Rhodium complex **208** has also been prepared by reaction with Wilkinson's catalyst and was found to contain a butatriene bent by ca. 30° .¹⁰⁷

In 1981, Sziemias and co-workers reported a truly extraordinary synthesis of 1,2,3-cycloheptatriene (**199**)



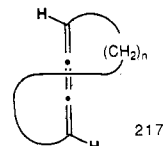
as a transient intermediate.¹³ Fluoride-induced elimination from **209** generates pyramidalized olefin **210**, itself a highly strained molecule, which may be trapped by cycloaddition with 9-methoxyanthracene (**215**). An unexpected minor product was diene **214**, the relative yield of which increased at decreasing concentrations of **215**. Sziemias attributed this result to rearrangement of **210** to **199**, perhaps via carbene **211**. In further experiments, the butatriene was trapped with numerous cyclic and acyclic dienes, as well as dipolar species such as phenyl azide.¹⁴ The regiochemistry of these additions is predictable, since addition to a terminal bond of **199** would afford a strained allene.

A similar approach was attempted without success for the synthesis of 1,2,3-cyclohexatriene.¹⁰⁸ Bicyclobutane **215** yielded only the adduct of **216** with di-

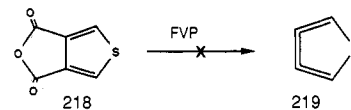


phenylisobenzofuran. Sziemias noted that decreased exothermicity of the $216 \rightarrow 200$ rearrangement (relative to $210 \rightarrow 199$), an observation consistent with strain estimates of 61 and 32 kcal/mol for **200** and **199**, respectively.¹⁵

Many other simple cyclic butatrienes remain unknown. For example, there are no reported examples of *trans*-cyclic butatrienes (**217**), which are analogous

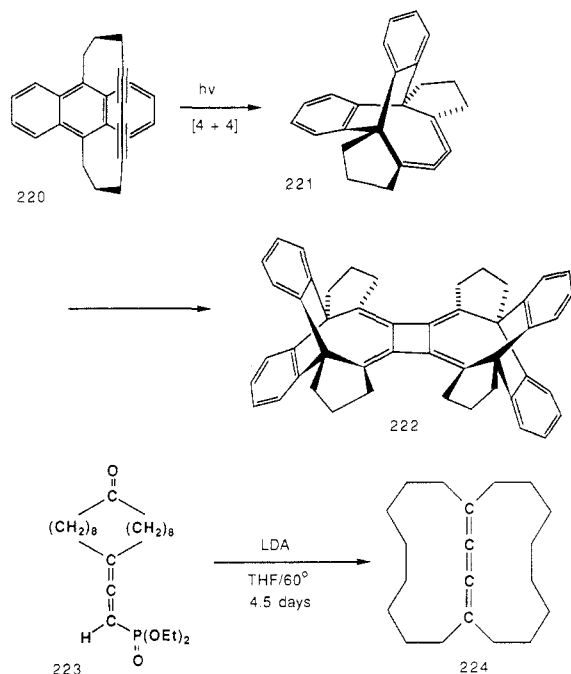


to *trans*-cycloalkenes. Dreiding models suggest that *trans*-1,2,3-cycloundecatriene might be made. 1,2,3-Cyclooctatriene (**198**) is still unknown but should be amenable to synthesis. This strongly bent butatriene may be too reactive to be isolated. Not surprisingly, there appear to be no examples of 1,2,3-cyclopentatrienes. One approach might be through 1,2-elimination reactions. However, Reinecke reported evidence that **219** is *not* formed upon pyrolysis of **218**.¹⁰⁹



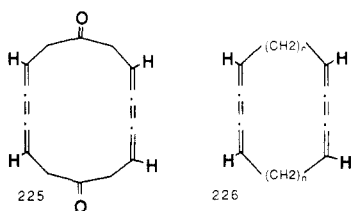
Several more complex cumulenes have been reported. Mataga and co-workers reported¹¹⁰ that irradiation of anthracenophane **220** yielded a cyclic butatriene (**221**), observed by UV spectroscopy at 77 K, which dimerized to the radialene **222**. This is an intriguing result because it shows that strained butatrienes might dimerize to radialenes. Such dimerization is also known in some acyclic butatrienes.

More recently, Macomber and Hemling reported the first simple bicyclic butatriene (**224**).¹¹¹ This symmetric

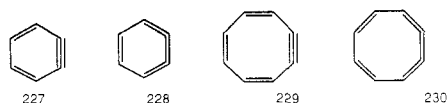


structure was prepared in modest yield by an intramolecular Horner–Emmons–Wittig reaction of **223**. The structure was supported by ^{13}C NMR resonances at 159.6 and 115.3 ppm and a λ_{max} at 268 nm. This structure type clearly deserves further exploration. Butatriene **224** probably is minimally strained; it is possible to construct models of a bicyclic butatriene with two fused nine-membered rings as the probable limiting ring size here.

Bisbutatrienes are not well-known. Diketone **225** was reported by Sondheimer and co-workers in 1973.¹¹² This should not be highly strained. Smaller structures such as **226** ($n = 1, 2$) seem feasible based on molecular models.



One very remarkable class of structures is that in which alkynes and butatrienes exist as apparent “resonance” structures.^{113–115} The simplest examples are benzyne (**227**) and didehydrocyclooctatetraene (**229**),



each of which might exist as a cyclic butatriene or cyclic alkyne. It is tempting to dismiss these as simple Kekulé resonance structures, yet each implies a very different molecular geometry and conformation. Remarkably, Dewar and Merz have reported that the MNDO method predicts discrete energy minima for alkyne **229** and cumulene **230**, with **229** 8.3 kcal/mol more stable.¹¹⁴ Their interconversion involves an orbital crossing, and hence a finite barrier is predicted. The known chemistry of **229** is consistent with an alkyne.¹¹³ Dewar and Merz’s prediction is provocative, but it is also possible that calculations which include correlation energy and

better model diradical character would show no minimum for cumulene **230**.

Benzyne is a better known example of the same question. Various groups have argued for cumulene- or alkyne-like structures.¹¹⁵ The best ab initio calculations appear to favor a “cumulene-like” structure.^{115d} In this case, it seems unlikely that two separate minima could exist.

IV. Conclusions

During the past several decades, an enormous variety of highly strained organic substances have gradually evolved from “impossible” to “probable” to “known”. Strained cumulenes and heterocumulenes, which are among these, comprise a class of fundamental substances in which relatively modest strain results in high reactivity. For example, 1,2-cyclooctadiene (**11**), which is predicted to have only ca. 14 kcal/mol of total strain energy, is not isolable. Many cyclic cumulenes seem best considered as reactive intermediates. In the allene series, several 1,2-cyclohexadienes have been generated as reactive intermediates, while the current limit for isolability is a buttressed 1,2-cyclooctadiene (**45**). There is convincing evidence that highly strained 1,2-cyclohexadiene (**9**) exists as a chiral allene. For more easily bent heteroallenes, there are several examples (**194**, **195**) of isolable six-membered-ring structures. The potential interconversion between cyclic allenes and carbenes has been considered for fully conjugated five-, seven-, and nine-membered rings. 1,2,4,6-Cycloheptatetraene (**80**) is well characterized but appears to interconvert with isomeric carbene **79**. Among cyclic butatrienes, 1,2,3-cycloheptatriene (**199**) could be generated and trapped, while 1,2,3-cyclononatriene (**197**) has been isolated.

In future studies, there is a great deal more to be learned about the synthesis, structural limitations, and properties of these novel substances. Improved structural data are more accurate estimates of strain energy are needed. Many fundamental structure types, such as bridgehead allenes (**153**), trans-cyclic butatrienes (**217**), 1,2-cyclopentadiene (**8**), and 1,2,3-cyclohexadiene (**200**) are excellent targets for synthesis. Synthetic applications of strained cumulenes remain virtually unexplored but offer many possibilities, perhaps most notably in cycloaddition chemistry. As one example, readily available 1,2-cyclooctadiene (**11**) should prove to be a versatile eight-membered-ring synthon. One intriguing reaction that bears further scrutiny is the “dehydro Diels–Alder”, which might involve 1,2-cyclohexadiene intermediates.

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