Bicyclo[*n*.1.0]alkenes

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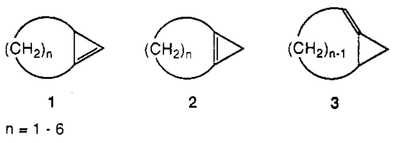
I. Introduction

Small-ring cycloalkenes arouse considerable interest because their energy content relative to their acyclic counterparts often results in unexpected properties. The cyclopropenes are especially interesting in this regard since the high strain energy ($\sim$54 kcal/mol) leads to unusual reactions, including isomerization to species normally considered to be high-energy ones (carbenes). The cyclopropenes thus represent one of the cornerstones of modern chemistry by virtue of their high strain and the unusual bonding properties that result therefrom.

In this paper we provide a review of the cyclopropenes of type **1** and **2** and the isomeric compounds of type **3** where $n \leq 6$. An earlier review discussed both **1** and **3** in terms of Bredt's rule.[1] Recent reviews cover the general area of cyclopropene chemistry.[2] This contribution covers *Chemical Abstracts* through Jan 1, 1989.



II. 1,3-Bridged Cyclopropenes

Cyclopropenes fused to carbocyclic rings as in **1** have been shown to be stable isolable compounds when $n \geq 6$. The elegant work of Eicher and Böhm represents one of the early entries into this field.[3] Thus 9-phenylbicyclo[6.1.0]non-1(8)-ene (**4**) could be isolated in 17% yield from the products resulting from the decomposition of **5** as illustrated in Scheme 1. This route can also be used to prepare simple cyclopropenes as well as higher derivatives of **4**.

Suda found that 9,9-difluorobicyclo[6.1.0]nonane (**6**) could be treated with *n*-butyllithium or methyllithium to yield cyclopropenes **7** and **8**, respectively.[4] These results can be interpreted in terms of the reactions shown in Scheme 2. The addition of alkyllithium reagents to cyclopropenyl double bonds is a well-established process.[5]

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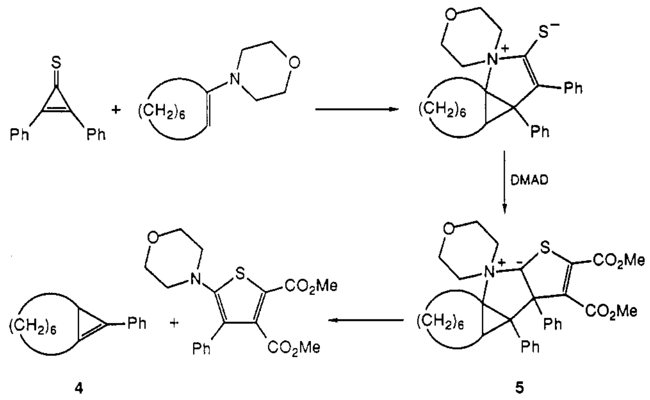
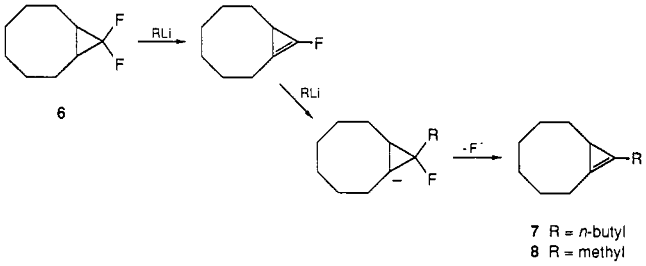
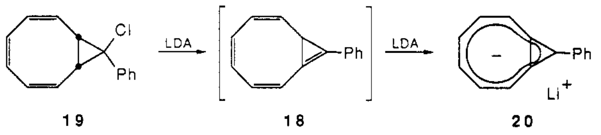


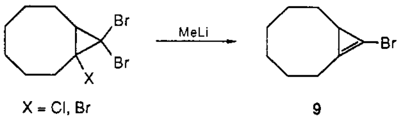
SCHEME 2



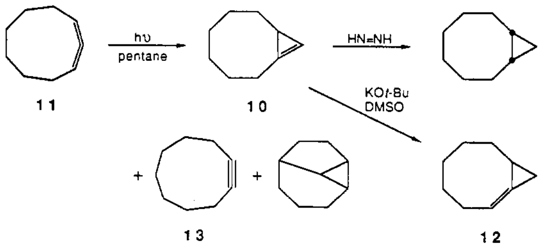
SCHEME 3



More recently, Baird and co-workers investigated the reactions of trihalocyclopropanes with methyllithium.[6] These compounds can be dehalogenated with methyllithium, and in several instances the product is a 1-halocyclopropene. Cyclopropene **9** can be purified by rapid column chromatography over alumina and kept at 0 °C in solution, but decomposes rapidly when neat.



The parent hydrocarbon **10** can be isolated as the major product from the singlet photochemistry of 1,2-cyclononadiene (**11**).[7] Compound **10** is remarkably



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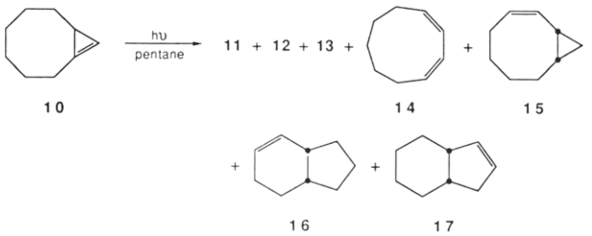
stable and can be purified readily by preparative column chromatography. Diimide reduction yields bicyclo[6.1.0]nonane, whereas brief treatment with potassium *tert*-butoxide in dimethyl sulfoxide affords isomer **12** in high yield.[7a]

Photolysis of pure **10**, which absorbs weakly up to 240 nm, in pentane leads to the starting allene **11** as well as products **12**–**17**.[7]



Cyclopropene **18** has been postulated as an intermediate when **19** is treated with lithium diisopropylamide in tetrahydrofuran at −70 to 0 °C.[8] Anion **20** was obtained as a thermally stable, deep reddish purple solution under these conditions (Scheme 3).

The lower homologue **21** and several derivatives have been synthesized as transient intermediates. Compound **22** can be generated as described earlier for **9** and trapped by *tert*-butyl mercaptan (Scheme 4).[6b] The cyclopropene is too unstable to be isolated as the pure compound at 20 °C.

Compound **21** itself has recently been prepared[9] from **23** by the vacuum gas–solid reaction (VGSR) technique[10] in which fluoride ion is deposited on glass helices to effect the elimination of β-halocyclopropylsilanes.[11] Diels–Alder addition of **21** to 1,3-butadiene gives the interesting compound **24** (Scheme 5). Although the thermal chemistry of **21** has not been elucidated completely, a major fate appears to be dimerization via an ene reaction.

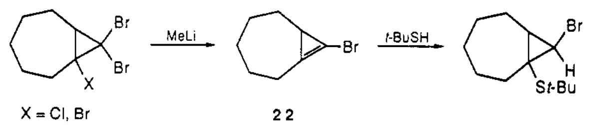
The reactive cyclopropene **25** appears to be an intermediate in the reaction of **26a** and **26c** with potassium *tert*-butoxide, whereas **26b** is unreactive under the same conditions.[12] Thus an attempt to generate homocycloheptatrienylidene by dehydrohalogenation of 8-chlorobicyclo[5.1.0]octadiene (**26a**,**b**) led instead to cyclooctatetraene, styrene, and heptafulvene as illustrated in Scheme 6.

A plethora of bicyclo[4.1.0]hept-1(7)-ene derivatives have been postulated as reactive intermediates in the reaction of 7,7-dihalobicyclo[4.1.0]heptane and related systems with strong base.[13] Under the reaction conditions these compounds usually either react by addition of the nucleophilic base to the strained double bond or undergo base-catalyzed prototropic rearrangement to less strained alkenes resulting from escape of the cyclopropenyl double bond into the six-membered ring.

7-Chloro derivative **27** was generated by Chan and Massuda when **28** was treated with cesium fluoride in tetrahydrofuran (Scheme 7, path a).[14a] The cyclopropene can be trapped with 1,3-diphenylisobenzofuran. When **27** is generated by the VGSR technique, 2-chlorocycloheptadiene can be isolated in 83% yield (Scheme 7, path b).[14b] This observation requires the intermediacy of carbene **29**, which would result from the cleavage of the central bond of **27**.

The parent hydrocarbon (**30**) can be synthesized by passing **31** through a "fluoride column" (VGSR technique).[10] With this technique, the neat product can be separated from the coproduct trimethylsilyl fluoride and isolated at −100 °C. The cyclopropene can be isolated in 85% yield as a Diels–Alder adduct of cyclopentadiene (Scheme 8).[11] In the absence of trapping reagents **30** undergoes an ene reaction above −90 °C to yield **32**.[15] This spectroscopically detectable adduct (NMR) rearranges readily in solution at 25 °C to yield the stable dimer **33**. The rearrangement is thought to

SCHEME 4



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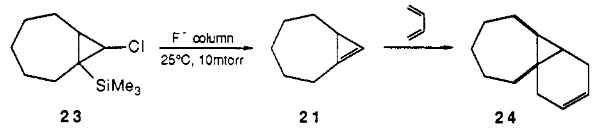

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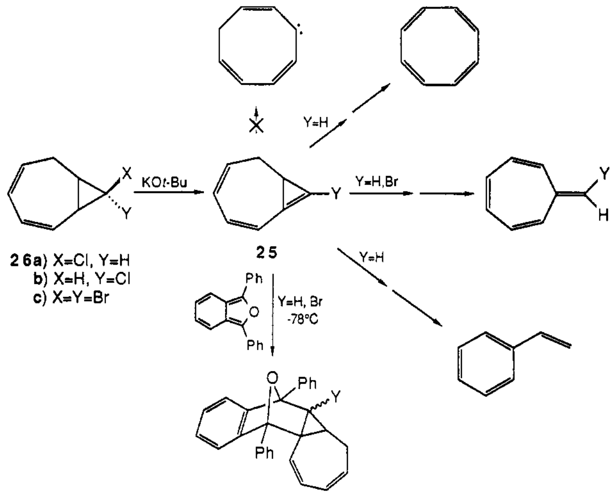

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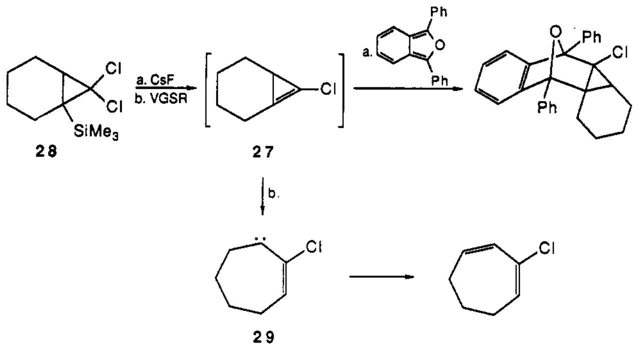

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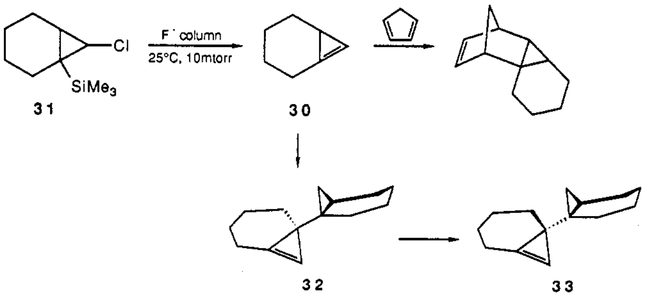

proceed via vinyl carbene intermediates. At room temperature tetramers provisionally identified as [2 + 2] dimers of **32** can be isolated.

The high strain energy and the expected propensity of **34** to dimerize via the facile ene reaction described above for **29** suggest that spectroscopic detection of the parent hydrocarbon **34** may be difficult. Nevertheless,

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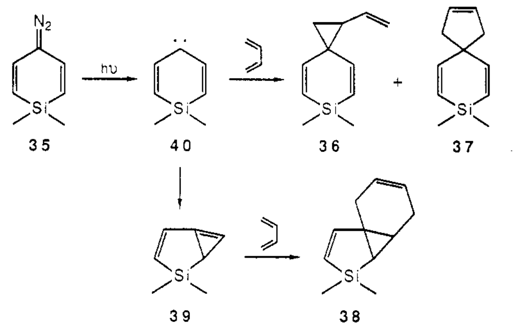
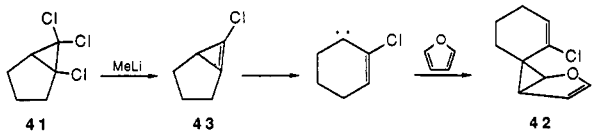
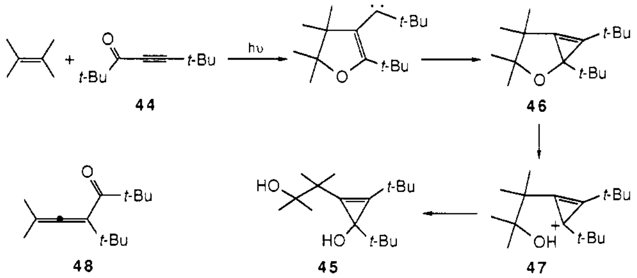


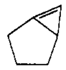
SCHEME 10



SCHEME 11



several derivatives of **34** have been generated and trapped.



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Photolysis of diazo compound **35** in the presence of 1,3-butadiene yielded products **36**–**38**.[16] The isolation of **38** can be taken as evidence for cyclopropene **39**, which could arise from the cyclization of vinyl carbene **40** (Scheme 9).

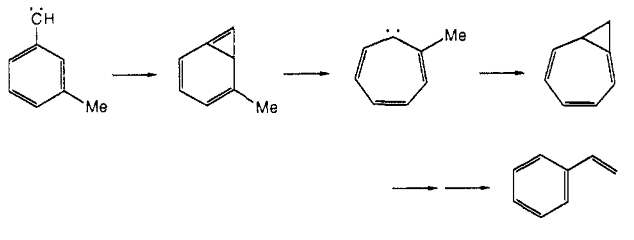
Trichloride **41** reacts with methyllithium in ether at 25 °C in the presence of furan to give **42**.[6b] The isolation of **42** can be explained by postulating the intermediacy of cyclopropene **43** followed by ring opening to the carbene (in strict analogy to **27** → **29**), which would be trapped by the furan (Scheme 10).

Photolysis of a mixture of tetramethylethylene and alkynone **44** in wet benzene results in the formation of cyclopropenol **45**.[17] The fused cyclopropene intermediate **46** has been invoked to account for this product (Scheme 11). Protonation of **46** followed by ring cleavage would give cyclopropenium ion **47**, which then adds hydroxide ion to provide **45**. Thermal fragmentation of **45** at 150 °C results in reclosure to **46**, which then formally expels dimethylcarbene to give allenic ketone **48**.

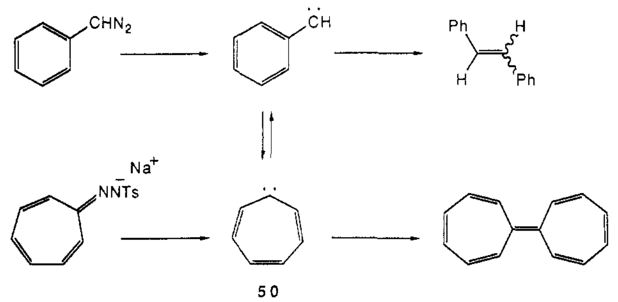
III. Bicyclo[4.1.0]hepta-2,4,6-trienes

Bicyclo[4.1.0]hepta-2,4,6-triene (**49**) and its derivatives constitute a group of cyclopropenes related to **1** with regard to the position of the cyclopropenyl double bond. Although an exhaustive review of this area is beyond the scope of this report, a few salient discoveries are adumbrated below.

SCHEME 12

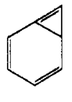


SCHEME 13



Unlike the well-characterized, stable bicyclo[4.1.0]hepta-1,3,5-trienes (benzocyclopropenes),[13b,18] these compounds can be regarded as reactive intermediates. Vander Stouw and Shechter first postulated the possible intermediacy of a bicyclo[4.1.0]heptatriene in 1964 to account for the formation of styrene in the gas-phase pyrolysis of *o*-tolyldiazomethane as exemplified in Scheme 12.[19] The cyclization of vinylmethylene to cyclopropene provided precedent for this mechanism.[20]

A flurry of activity in this area has revealed the intricate multiple carbene rearrangements that arise as a consequence of the ring-expansion rearrangements in the arylcarbene series.[21-31] Although these rearrangements have been found to occur both in the gas phase and in solution, the interconversions that occur in solution seem to be simpler and thus better understood. The roles of bicyclo[4.1.0]hepta-2,4,6-triene (**49**), cycloheptatrienylidene (**50**), and 1,2,4,6-cycloheptatetraene (**51**) in these C_7H_6 rearrangements have been delineated somewhat. On the basis of the isolation of heptafulvene from the thermolysis of phenylcarbene and from the thermolysis or photolysis of tropone tosylhydrazone sodium salt, Jones argued for cycloheptatrienylidene (**50**) as the key intermediate in the ring expansion of phenylcarbene.[22] Wentrup established the reversibility of the ring expansion by isolating stilbenes from the thermolysis of tropone tosylhydrazone sodium salt.[24] Wentrup also considered the ring-expansion reaction of phenylcarbene to occur directly rather than through a bicycloheptatriene intermediate (Scheme 13).[37b]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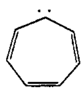
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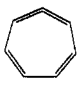
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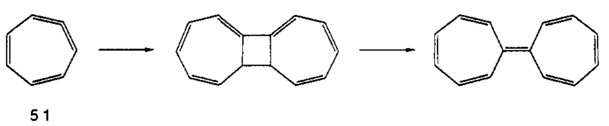
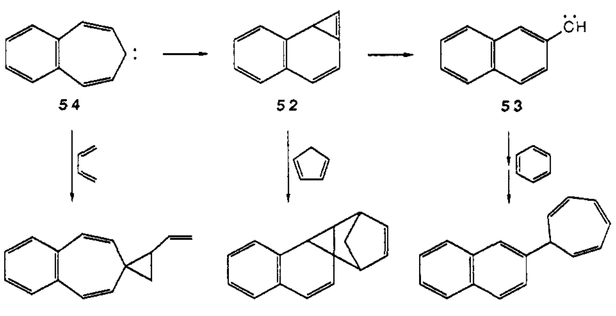
More recent spectroscopic studies as well as chemical evidence also rule out bicyclo[4.1.0]hepta-2,4,6-triene (**49**) and suggest that 1,2,4,6-cycloheptatetraene (**51**) plays the pivotal role in these rearrangements.[33-35] Deuterium-labeling studies reveal that the intramolecular chemistry of cycloheptatetraene involves reversible thermal or photochemical equilibrium with phenylmethylene.[33] The intermolecular chemistry involves dimerization at temperatures as low as 10 K to form a labile [2 + 2] dimer that undergoes a thermally allowed rearrangement to give heptafulvene upon warming to room temperature (Scheme 14). Untch also observed that dehydrochlorination of a mixture of chlorocycloheptatrienes yields the same products.[36]

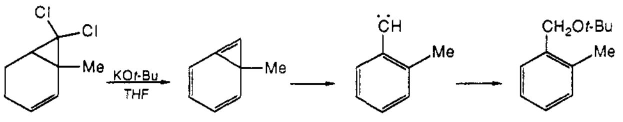
SCHEME 14



SCHEME 15

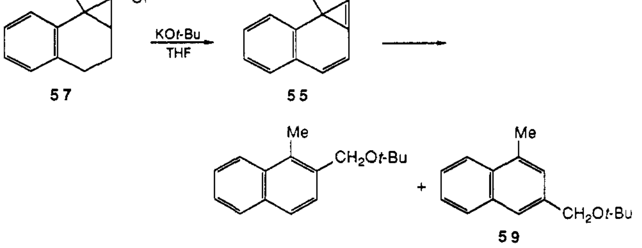


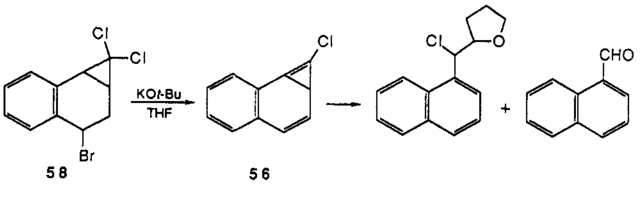
Despite the lack of evidence for cyclopropene intermediates in these reactions, simple bicycloheptatrienes have been generated by dehydrochlorination–isomerization reactions of *gem*-dichlorocyclopropanes.[32] The bicycloheptatriene generated under the reaction conditions rearranges to the arylcarbene. Products that might arise from ring expansion could not be isolated.



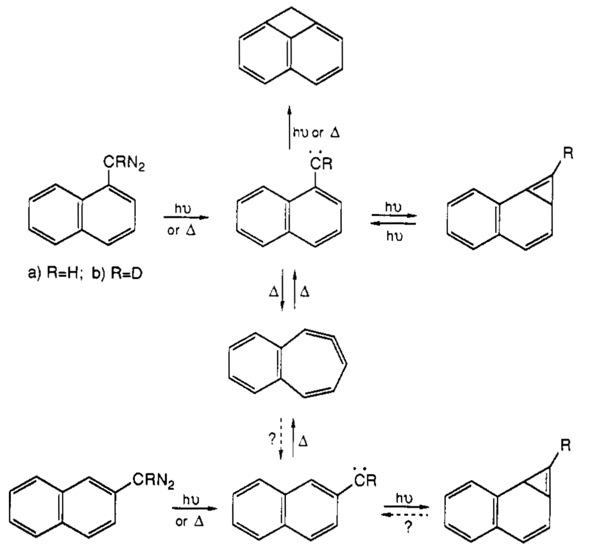
Evidence for the discrete existence of benzobicyclo[4.1.0]hepta-2,4,6-trienes is considerably more secure.[21] Trapping experiments have produced Diels–Alder adducts of 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**52**) as well as 2-naphthylcarbene (**53**) and 4,5-benzocycloheptatrienylidene (**54**) as illustrated in Scheme 15.[30a]

Evidence for both 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene **55** and 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene **56** can be found when **57** and **58**, respectively, are treated with potassium *tert*-butoxide in tetrahydrofuran.[32] The isolation of **59** from **55** would require a ring-expansion reaction.

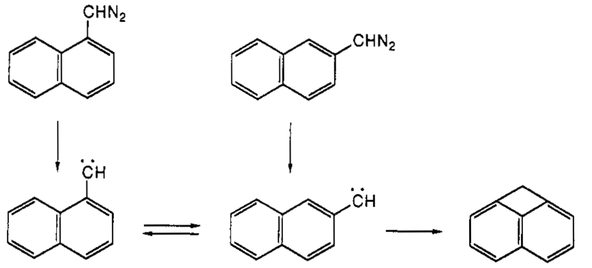




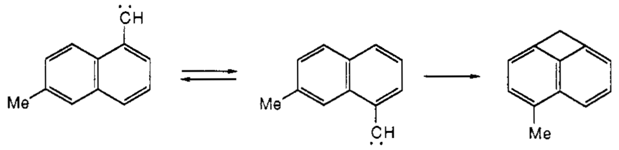
SCHEME 16



Additional evidence for arylcarbene interconversions (and thus possibly cyclopropene intermediates) in the naphthalene series was provided by Becker and Wentrup, who showed that vacuum pyrolysis of 1- and 2-naphthyldiazomethane yielded cyclobuta[*de*]naphthalene by insertion of the carbene into a peri-C–H bond.[37]



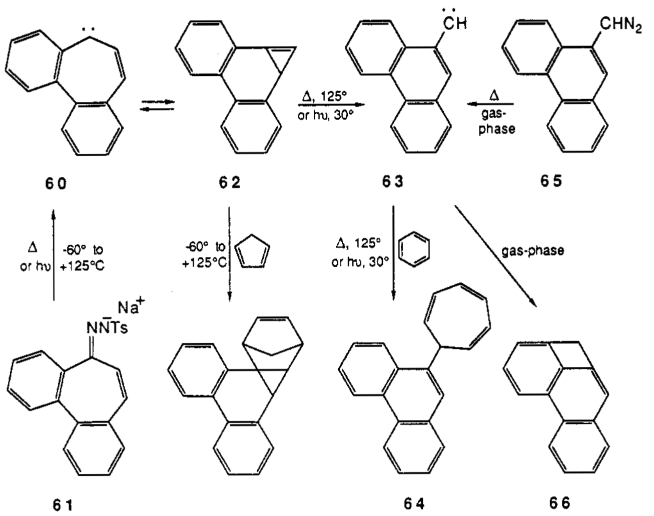
Engler and Shechter made analogous observations by demonstrating that (6-methyl-1-naphthyl)methylene rearranges thermally to the isomeric (7-methyl-1-naphthyl)methylene, presumably via two isomeric 2-naphthylmethylene intermediates.[38]



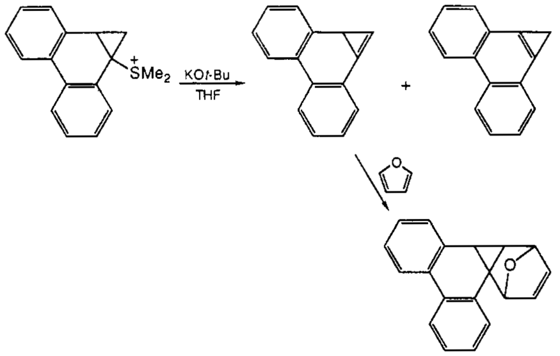
Spectroscopic detection of benzobicyclo[4.1.0]hepta-2,4,6-trienes was provided by Chapman and co-workers in 1986.[39] These results are summarized in Scheme 16. Irradiation of the naphthyldiazomethanes matrix isolated in argon at 15 K yielded, in each case, the benzobicyclo[4.1.0]hepta-2,4,6-triene. The photochemistry of the naphthyldiazomethanes thus contrasts sharply with that of phenyldiazomethane, which gives 1,2,4,6-cycloheptatetraene. Flash vacuum thermolysis of the naphthyldiazomethane followed by matrix isolation of the pyrolysate produces a common product, tentatively identified as 4,5-benzobicyclo[4.1.0]hepta-1,2,4,6-tetraene.

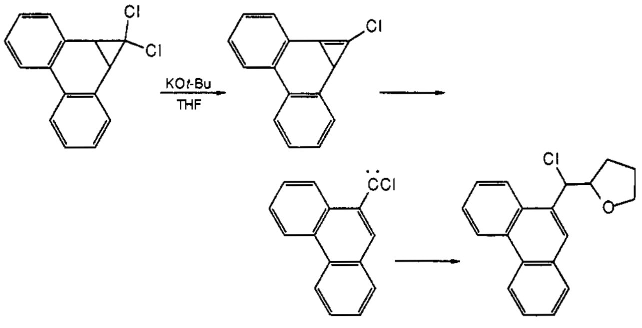
Evidence for the existence of dibenzobicyclo[4.1.0]hepta-2,4,6-trienes as discrete intermediates has also been presented. For example, carbene **60**, generated from tosylhydrazone **61**, isomerizes to **62**, which can be trapped with cyclopentadiene.[30] In the absence of trapping reagents **62** rearranges to phenanthrylcarbene **63** (Scheme 17). When this process is carried out in benzene, compound **64** is produced; however, when **63** is generated in the gas phase from **65**, cyclobutaphenanthrene **66** resulting from insertion of the carbene into a peri-C–H bond is produced.[21d,37]

SCHEME 17



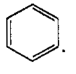
Additional evidence for these species can be found in the following elimination reactions.[30b,32,40–42]





IV. Bicyclo[3.1.0]hexa-1,3,5-trienes

Diyl species **67** results formally from the removal of two hydrogen atoms from the meta positions of benzene. This species is referred to frequently as *m*-benzyne in analogy with *o*-benzyne. Although evidence for the diradical has been presented in only one instance for simple benzene derivatives,[43] there is a considerable body of evidence for the isomeric bicyclo[3.1.0]hexa-1,3,5-triene form (**68**).



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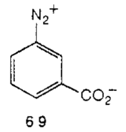
68

Numerous theoretical calculations at various levels of sophistication have focused on the dehydrobenzenes. Simple Hückel calculations, when applied in conjunction with Hess and Schaad's semiempirical approach,[44] reach relatively reliable conclusions concerning the aromaticity of *m*-benzyne. With the resonance energy per π electron (REPE) value of 0.065 for benzene as a standard, the REPE for **68** is 0.055.[44,45] Thus replacement of H_1 and H_3 of benzene with a σ bond is predicted to generate an aromatic hydrocarbon.

Early theoretical studies had predicted the singlet–triplet gap of *m*-benzyne to be small. Using extended-Hückel calculations, Hoffmann predicted the ground state to be a singlet.[46] From ab initio studies, Wilhite predicted **68** to be a triplet.[47] Both of these studies, however, were hampered owing to the consideration of only the benzenoid structure **67**. A geometry optimization study by Washburn and McKelvey assumed **68** to be planar and to possess C_{2v} symmetry.[48] The singlet bicyclohexatriene was predicted to be the ground state with the optimum singlet structure best described as a reasonance-delocalized bicyclo[3.1.0]hexatriene with a bridging bond of 1.5 Å. In a similar study of the dehydrobenzenes, Dewar and co-workers concluded that **68** should exist as a singlet species containing a long bridging σ bond between C_1 and C_5.[49] Noell and Newton also calculated **68** to exist in the singlet ground state.[50] Whereas Washburn found no energy barrier for the collapse of diradical **67** to bicyclic **68**, Dewar calculated **68** to be separated from **67** by a barrier of 9 kcal/mol.[49b] As might be expected, theoretical treatment of **68** predicts π polarization analogous to that of an azulenoid hydrocarbon.

Despite the unusual geometry of **68**, the total calculated strain is not prohibitive. From Benson group equivalence tables,[51] the $\Delta H_f°$ is predicted to be +41.5 kcal if strain and resonance contributions are ignored. The latter are estimated to be +17 kcal by extrapolation of the REPE values based on a resonance energy of benzene of 21 kcal. With Dewar's predictions of ΔH_f of **68** to be 118 and 147 kcal,[49] the strain would be 93 and 123 kcal, respectively. The ab initio calculations of Washburn predict ΔH_f of **68** to be 145 kcal, containing 121 kcal of strain.[48] The 90–125 kcal of strain predicted for bicyclo[3.1.0]hexatriene is not excessive when compared with the 101 and 116 kcal of strain measured for benzvalene and prismane, respectively.[52] Thus in view of the above calculation, the unusual geometry of **68** should not induce excessive strain that would preclude its existence.

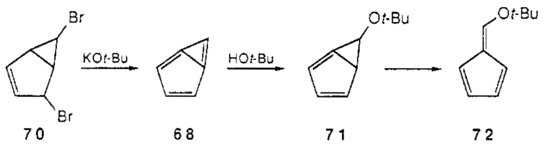
Flash vacuum photolysis of the diazonium salt **69** formed from *m*-aminobenzoic acid gave a transient intermediate that was shown by mass spectroscopy to be an *m*/*e* 76 species (C_6H_4).[53] The UV spectrum was not interpretable in terms of **67** or **68**. Attempts to extend this approach to solution chemistry were inconclusive with regard to structure.[54]



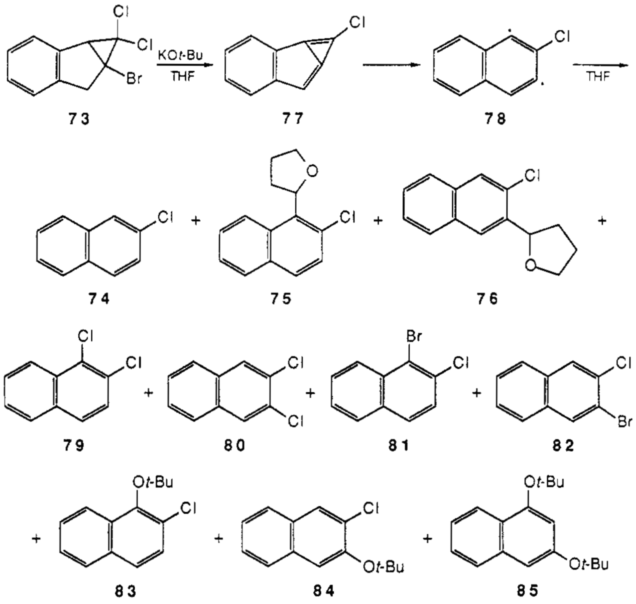
69

Compelling evidence for the discrete bicyclohexatriene structure was finally presented by Washburn, Zahler, and Chen;[55] thus base-catalyzed elimination of HBr from **70** results in the formation of **68** (Scheme 18). Compound **68** is trapped by the base to give **71**, which then rearranges to the fulvene **72** as an isolable product. Deuterium- and ^{13}C-labeling studies support the intermediacy of **68** and not **67** in this reaction.[55] Introduction of a *tert*-butyl or methyl group at C_2 of **70** provided the respective C_2-alkylated derivatives of **68**.[55a,56]

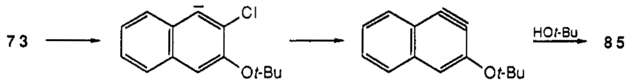
SCHEME 18



SCHEME 19



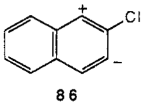
SCHEME 20



In contrast, the benzologue **73** undergoes base-induced elimination in tetrahydrofuran to yield a complicated mixture of naphthalenes, at least part of which (**74**–**76**) would appear to arise from the intermediate **77** opening to the diyl **78** followed by hydrogen atom extraction from tetrahydrofuran (Scheme 19).[57]

The remaining naphthalenes, **79**–**85**, are thought to arise from nucleophilic addition either directly to **77** or to polar intermediates. Nucleophilic addition across the bridging bond in **77** via the zwitterions **86** and **87** would account for **79**–**84**. Compound **85** could then arise as illustrated in Scheme 20.

Although zwitterions **86** and **87** might normally be considered as high-energy species, they could, in principle, arise from a cyclopropene → vinyl carbene rearrangement of **77**. The zwitterions, which might be regarded as resonance structures of **88**, would allow the naphthalenes to regain resonance energy.



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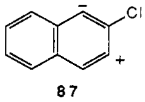

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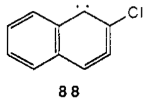
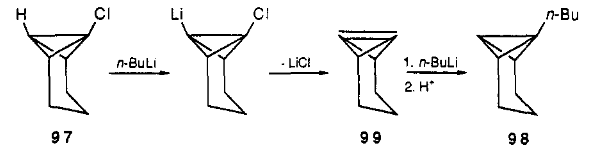
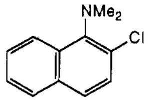


88

SCHEME 21



It is interesting that the reaction of **73** with potassium *tert*-butoxide in tetrahydrofuran in the presence of dimethylamine (conditions of Washburn)[55] yielded mainly **89–91**, suggesting that the nucleophilic amide traps the ionic species to the exclusion of the diyl.



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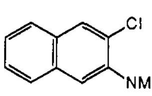

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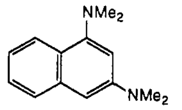

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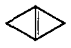
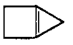
V. 1,2-Bridged Cyclopropenes

Compounds that incorporate the features of **1–3** are unknown in the case of the parent compounds **92–96**.

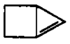


92

93



94



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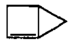
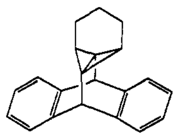


96

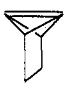
Calculations indicate that significant pyramidalization of the double-bond carbons will lead to nonplanar structures for **92** and **94**.[58–61] This deviation from planarity enables the C–H bonds to overlap with the pure π orbital and thereby stabilize the conformation. Calculated heats of hydrogenation for these compounds show that **92** is more strained than **93** and that **94** is more strained than **96**, which in turn is more strained than **95**.[60,62–65] In a number of cases the cyclopropene is probably unstable relative to the unsaturated carbene.

Despite the pessimistic theoretical predictions some remarkable compounds that incorporate the structural features of **92–96** have been reported by Szeimes and co-workers. Thus addition of 1-chlorotricyclo[4.1.0.0^{2,7}]heptane (**97**) to an excess of *n*-butyllithium produced the substitution compound **98** in 87% yield.[66] Exhaustive control experiments demonstrated that **98** is formed via an elimination–addition mechanism as illustrated in Scheme 21. Evidence in support of this mechanism (and thus **99**) as opposed to a metal–halogen exchange or direct coupling was presented as follows: (1) the initially formed carbanion was trapped by D$_2$O; (2) the 7-methyl derivative of **97** was recovered unchanged under the reaction conditions;[66] and (3) **99** was trapped by anthracene as the Diels–Alder adduct **100**.[67]



100

The dehydrohalogenation approach was also used to prepare bicyclobutene derivatives **101–103**.[68,69]



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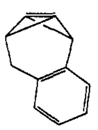
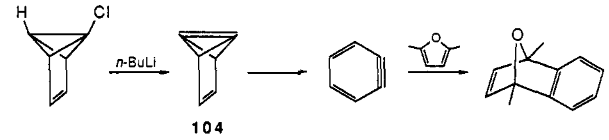


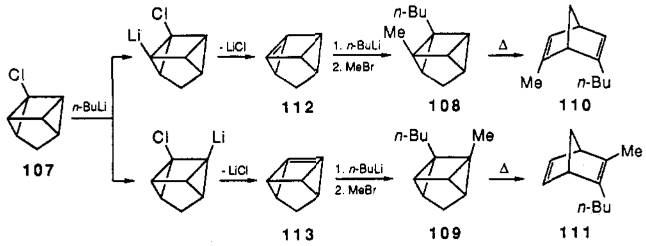
102

103

SCHEME 22



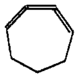
SCHEME 23



Fluoride-induced elimination of β-halo silane precursors has also been utilized successfully in the preparation of **99** and **101–103**.[69,70] Attempts to synthesize **92** and its methyl derivatives by the dehydrohalogenation method were unsuccessful.[71]

Compound **104**, on the other hand, isomerizes spontaneously to *o*-benzyne, which can be trapped with 2,5-dimethylfuran (Scheme 22).[72] The facile rearrangement of **104** indicates that the bridgehead double bond in this compound induces even more strain than the triple bond in benzyne.

A similar rearrangement to bent 1,2,3-trienes **105** and **106** is observed when **99** and **102** are generated above 20 °C.[69,70] Both of these compounds may be trapped with 1,3-dienes or 1,3-dipoles.



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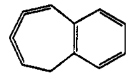


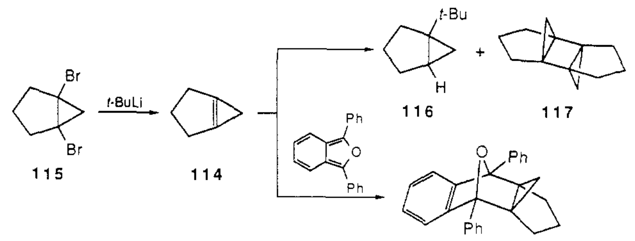
106

The Diels–Alder reaction of **99** and its analogues with dienes such as furan[73] and benzindole[74] derivatives provides a useful route to small-ring propellanes[75] containing the bicyclobutane moiety.[76] Due to the extreme susceptibility of the double bond of **99** and its analogues to undergo nucleophilic addition, it is possible to introduce bridgehead substitution in the bicyclobutane.[77,78] Use of sterically hindered nonnucleophilic bases[67,73,79] allows the introduction of thio and amino groups into the bridgehead position of the molecule.[76,80]

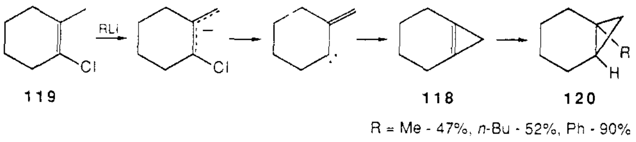
n-Butylmethylquadricyclanes **108** and **109** were isolated by Szeimes and co-workers in a 2:1 ratio when a mixture of 1-chloroquadricyclane (**107**) and *n*-butyllithium was quenched with methyl bromide (Scheme 23).[81,82] The mixture of **108** and **109** was then thermally converted to norbornadienes **110** and **111**. Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1(7)-ene (**112**), a derivative of **94**, was proposed as a reactive intermediate, formed by an elimination process analogous to the one described above for **99**. Additional evidence for the existence of **112** is given by the isolation of Diels–Alder products with anthracene and 2,5-dimethylfuran.[81,83]

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1(2)-ene (**113**), a derivative of **96**, was proposed as the other reaction intermediate (Scheme 23).[81] Although cycloaddition products of **113** could not be isolated, deuterium-labeling studies provide compelling evidence for the intermediacy of this reactive species.[82]

SCHEME 24



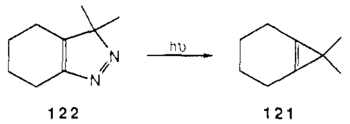
SCHEME 25



The formation and trapping of bicyclo[3.1.0]hex-1(5)-ene (**114**) from the corresponding *vic*-dibromide **115** have been described recently.[84] When **115** was treated with *tert*-butyllithium in THF or ether at −78 °C, a rapid reaction was observed. The major products were found to be 1-*tert*-butylbicyclo[3.1.0]hexane (**116**) and dimer **117** (Scheme 24). Compound **114** could be trapped as a Diels–Alder adduct with furan, 2,5-dimethylfuran, 1,3-diphenylisobenzofuran, or anthracene.

Bicyclo[4.1.0]hept-1(6)-ene (**118**) and its derivatives have been the object of several synthetic studies. Gassman proposed **118** as an intermediate in the reaction of 1-chloro-2-methylcyclohexene (**119**) with alkyllithium reagents (Scheme 25).[85] Deuterium labeling of the methyl group of **119** provided **120** deuterated at C_7, confirming the intermediacy of **118**.[85]

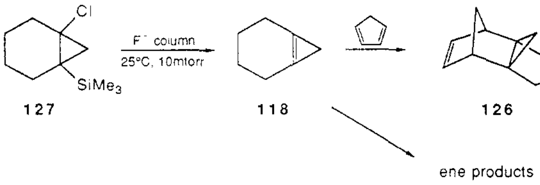
7,7-Dimethylbicyclo[4.1.0]hept-1(6)-ene (**121**), the only spectroscopically detectable derivative of **118**, was synthesized by Closs and co-workers.[86] The photolysis of 3*H*-pyrazole **122** at −60 °C in cyclopropane gave **121**, which decomposed above −35 °C. The ^{1}H NMR spectrum of **121** at −60 °C showed signals at δ 1.21 (s, 6 H), 1.7 (m, 4 H), and 2.3 (m, 4 H). The appearance of a singlet for the two methyl groups of **121** confirms that this compound is either planar or undergoing rapid inversion.



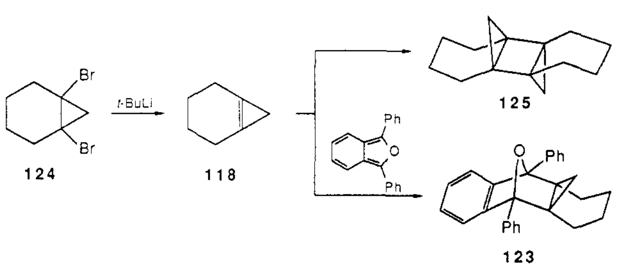
122 121

Subsequently, Wiberg and Bonneville reported that **118** could be isolated as Diels–Alder adduct **123** in the debromination of **124**.[84] In the absence of trapping reagent, **118** dimerizes even at −120 °C to give **125** (Scheme 26).

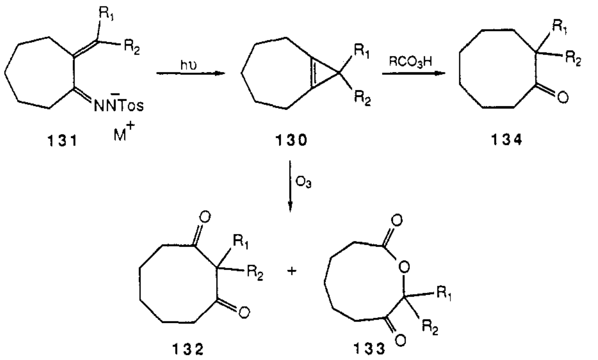
Billups and co-workers found that **118** could be isolated as Diels–Alder adduct **126** in the fluoride-induced trimethylsilyl halide elimination of the bicyclo[4.1.0]heptane **127**.[11] In the absence of cyclopentadiene, **118** dimerizes via an ene reaction.[87]



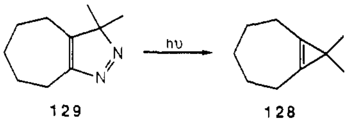
SCHEME 26



SCHEME 27



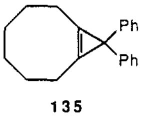
Closs and co-workers also prepared 7,7-dimethylbicyclo[5.1.0]oct-1(7)-ene (**128**) from 3*H*-pyrazole **129** by irradiation in *n*-pentane at 15 °C.[86b] The stability of **128** was tested by heating a solution of the hydrocarbon in fluorotrichloromethane to 100 °C for 10 h; no change was observed in the ^{1}H NMR spectrum.



129 128

The synthesis and epoxidation of 7,7-dialkylbicyclo[5.1.0]oct-1(7)-ene **130**, which was formed by irradiation of tosylhydrazone salt **131**, have been investigated by Friedrich and co-workers.[88] The cyclopropene reacted with ozone to give cycloocta-1,3-dione **132** and lactone **133** and with peracid to give cyclooctanone **134** (Scheme 27).

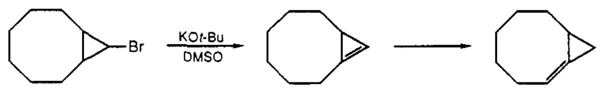
9,9-Diphenylbicyclo[6.1.0]non-1(8)-ene (**135**) has also been prepared[89] from cyclooctyne and diphenyldiazomethane using the Closs procedure.[86]



135

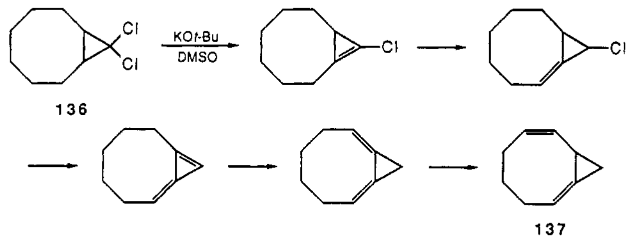
VI. Alkylidenecyclopropanes

Compounds of type **3** in which an eight- and three-membered ring are fused can be prepared readily by dehydrohalogenation of halo- and *gem*-dihalocyclopropanes as exemplified in the following reaction.[13a]

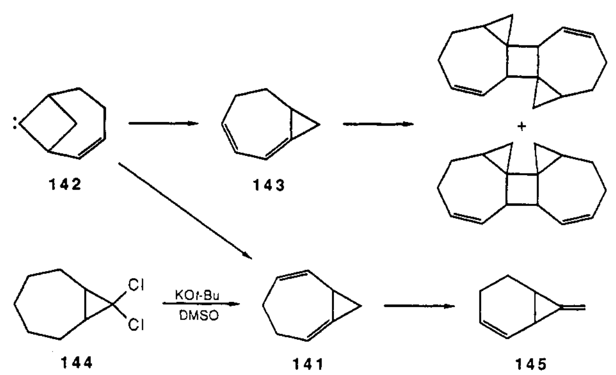


A further example is the conversion of **136** into **137**. The reaction is postulated to proceed through the series

SCHEME 28

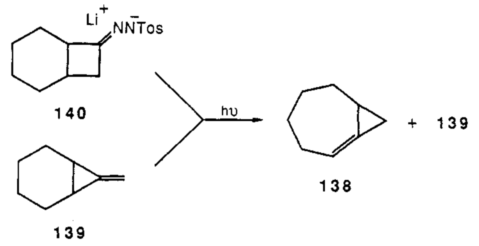


SCHEME 29

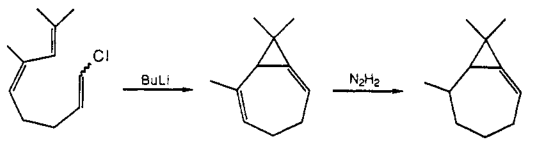


of strained-ring intermediates illustrated in Scheme 28.[90]

Bicyclo[5.1.0]oct-1(2)-ene (**138**) can be prepared along with **139** by pyrolysis of the dry lithium salt of tosylhydrazone **140**[91] or by photolysis of **139**.[92]



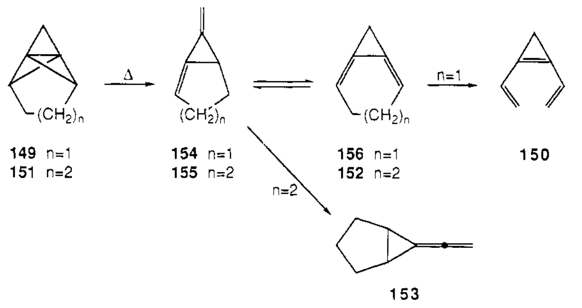
The extensive work of Köbrich and co-workers on the intramolecular cyclization of vinylidene carbenes has led to the synthesis of a large number of compounds in this series.[93]



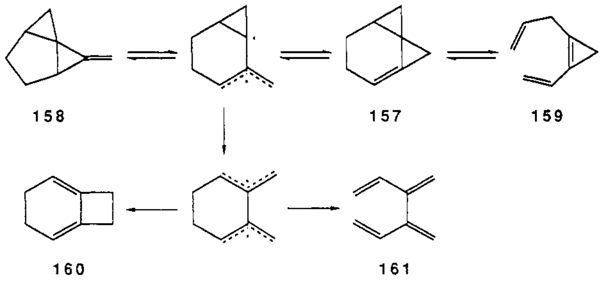
Compound **141** can be prepared from two very diverse sources (Scheme 29). Carbene **142**, generated by the Brinker gas-phase dehalogenation technique, rearranges spontaneously to a mixture of **141** and **143**,[94] whereas treatment of *gem*-dichlorocyclopropane **144** with strong base yields the same intermediate.[95] Compound **141** rearranges to the stable isomer **145** via a methylenecyclopropane rearrangement. Isomer **143**, produced in the Brinker synthesis, dimerizes to a mixture of cyclobutanes. The thermal chemistry of **145** has been investigated by both groups.

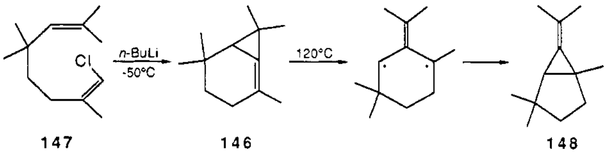
Although bicyclo[4.1.0]hept-1(2)-ene itself remains unknown, Köbrich and Baumann synthesized the pentamethyl analogue **146**, which was isolated in 20–30% yield by carbenoid cyclization of chloro olefin **147**.[93] Thermolysis of **146** at 120 °C produced methylenecyclopropane **148** through a trimethylenemethane intermediate.[96]

SCHEME 30



SCHEME 31



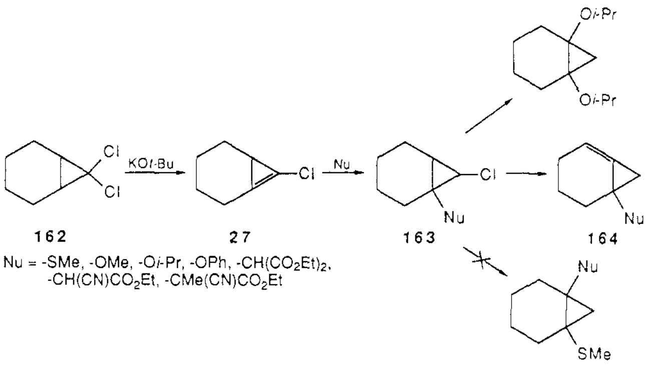


Thermolysis of [1.1.1]propellane **149** at 430 °C by Szeimies and Belzner led to the isolation of a single product, 1,2-divinylcyclopropene (**150**).[97] At 370 °C, propellane **151** was converted to a 3:2 mixture of diene **152** and allene **153** (Scheme 30). Retention of the central C–C bond of the [1.1.1]propellane framework can be recognized as a common feature in the isomerization of **149** and **151**. These are believed to open to the short-lived intermediates **154** and **155**, which then undergo a methylenecyclopropane rearrangement, affording the more stable dienes **152** and **156**. In the case of **156**, an electrocyclic ring-opening reaction occurs, giving **150**.

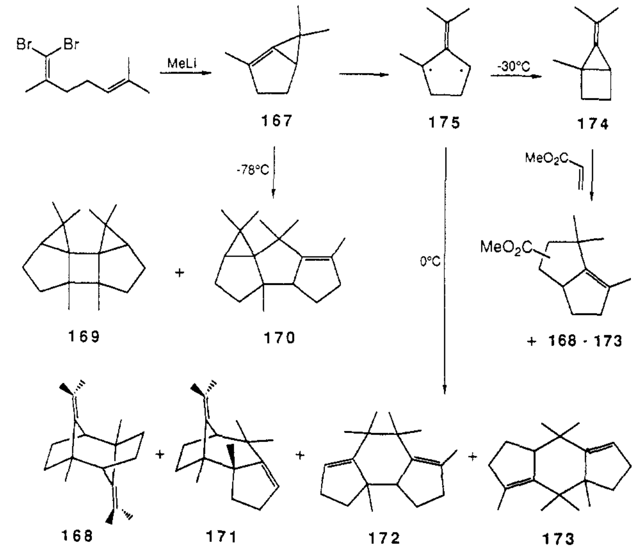
The unusual bicyclo[4.1.0]hept-1(2)-ene **157** as an intermediate of the thermal rearrangement of 2-methylenetricyclo[4.1.0.0^{1,3}]heptane (**158**) has been reported by two groups (Scheme 31).[98] At 150 °C **158** forms an equilibrium mixture with **157** and cyclopropene **159**; however, at 180 °C this mixture rearranges irreversibly into a pressure-dependent mixture of diene **160** and tetraene **161**.

Treatment of dichloride **162** with strong base (KO-*t*-Bu or KO-*i*-Pr) leads to **27** as a reactive intermediate.[13a,99] Nucleophiles add readily to the double bond of **27** to yield **163**. Whereas compound **163** (Nu = SMe) was inert to further reaction with base, for Nu = O-*i*-Pr, it was possible to isolate 1,6-diisopropoxybicyclo[4.1.0]heptane.[13a] In a number of other cases (Nu = ester), **163** underwent further elimination and isomerization to give bicyclo[4.1.0]hept-1(2)-ene **164** (Scheme 32).[99] The isolation of **164** is surprising since one might

SCHEME 32

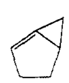


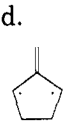
SCHEME 33



have expected the double bond to migrate to the 4(5) position.

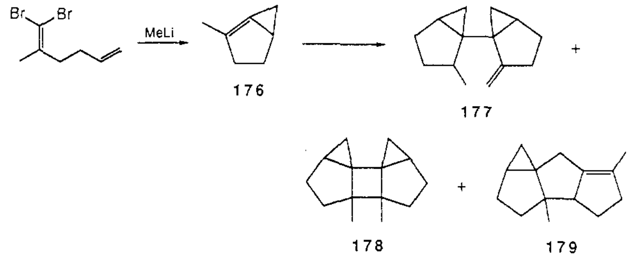
The bicyclo[3.1.0]hex-1(2)-ene (**165**) system has been the object of extensive investigations. As a bridged methylenecyclopropane system of type **3**, it would be expected to undergo thermal reaction to form the trimethylenemethane (TMM) **166**. Although **165** is unknown, several derivatives have been synthesized and their chemistry fully delineated.


165

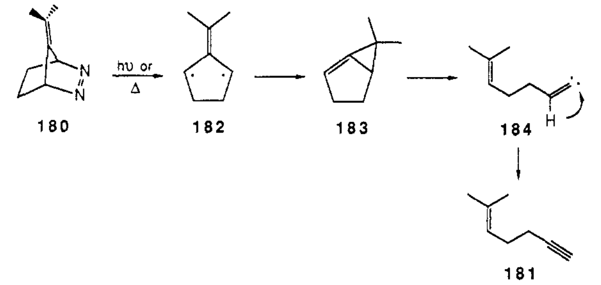

166

Köbrich and Heinemann provided the first evidence for the existence of 2,6,6-trimethyl derivative **167** by isolating the TMM dimer **168**.[100] Further work by Köbrich resulted in the isolation of the [2 + 2] dimer **169** and a dimer "of lower symmetry".[1] Berson and co-workers[101] confirmed the work of Köbrich and identified several other dimers (**170**–**173**).[102] The product mixtures were found to be strongly temperature dependent: at −78 °C only **169** and **170** are observed; at 0 °C **168** and **171**–**173** are isolated as the major hydrocarbons; at −30 °C, in addition to **168**–**173**, compound **174** is formed and trapped with methyl acrylate (Scheme 33). This dependence on temperature is consistent with the presence of a finite barrier to thermal dissociation of the C_5–C_6 bond of **167** to the TMM **175**. It was also found that relative to the TMM dimers **171**–**173**, the yield of bicyclo[3.1.0]hex-1(2)-ene

SCHEME 34



SCHEME 35



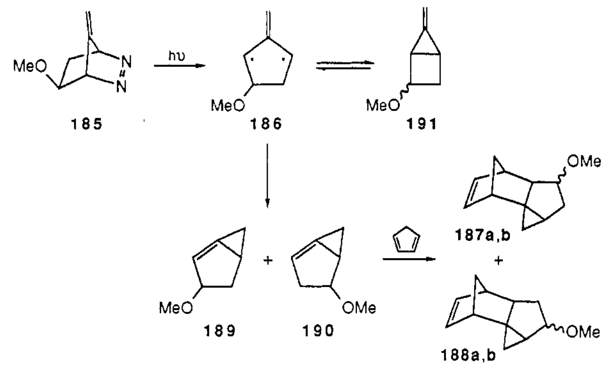
dimers **169** and **170** increases as the initial concentration of the dihalide reactant is increased. These observations are interpretable in terms of a competition between a bimolecular dimerization and a unimolecular ring opening.

The unimolecular/bimolecular competition also is strongly dependent on the substitution pattern of the bicyclo[3.1.0]hex-1(2)-ene system. Generation of the 2-methyl derivative **176** at −78 °C or at 0 °C yielded the three hydrocarbons **177**–**179** in a ratio of 5:2.5:1 (Scheme 34).[101a] Dimers **178** and **179** have structures homologous to **169** and **170**; dimer **177** is the product of an ene reaction between two molecules of **176**. The product ratio was found to be invariant with the concentration of dihalide reactant. In the case of **176**, dimerization competes with ring opening to a TMM more effectively than in the case of **167**. The reasons for this presumably include the bond-weakening effect of the *gem*-dimethyl substitution at C_6 in **167** and perhaps a steric retardation to dimerization. Only **176** was captured as a Diels–Alder adduct with 1,3-diphenylisobenzofuran in low yield.[101a]

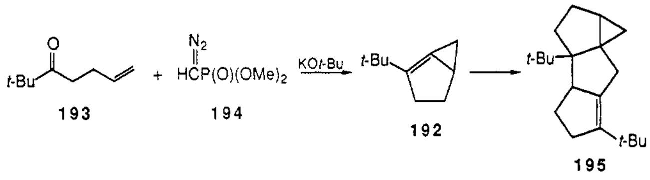
Photolysis of diazene **180** at 300 nm and 77 K with subsequent warming, or pyrolysis of **180** at 700 °C and 10^{-3}–10^{-4} Torr, yielded enyne **181** and numerous other products.[103] The formation of **181** involved the cyclization of biradical **182** to bicyclo[3.1.0]hex-1(2)-ene **183** followed by cycloreversion to carbene **184** and hydrogen shift (Scheme 35). Whereas **181** is the predominant photochemical product, the thermal reaction of **182** is bond cleavage to yield mainly a mixture of trienes, but cyclization to **183** is competitive.

Photolysis of diazene **185** yielded diyl **186**, which reacted with cyclopentadiene to give twelve products.[104] Eight of these adducts contained fused or bridged structures typical of TMM products. The remaining four adducts (**187a,b** and **188a,b**) are derived by Diels–Alder addition of cyclopentadiene to the strained double bond of methoxybicyclo[3.1.0]hex-1(2)-enes **189** and **190** (Scheme 36). Compounds **189** and **190** are believed to be formed from the bicyclo[2.1.0]pentane **191** by a rearrangement that has a practical threshold temperature above −40 °C. This transformation is an

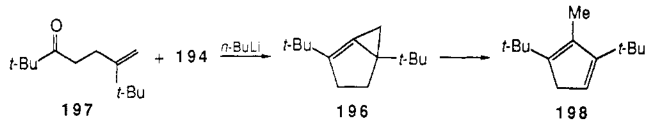
SCHEME 36



SCHEME 37



SCHEME 38



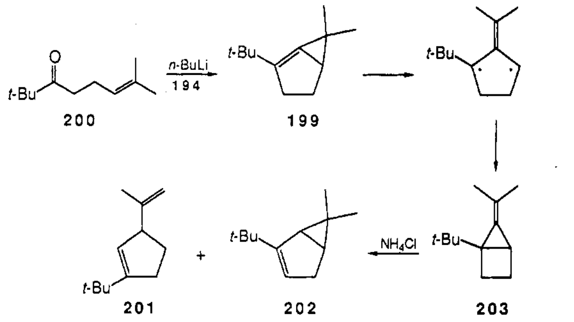
example of the reverse of the 5-alkylidenebicyclo-[2.1.0]pentane → bicyclo[3.1.0]hex-1(2)-ene rearrangement illustrated above.[101b]

The presence of bulky substituents on or near the strained double bond of a bicyclo[3.1.0]hex-1(2)-ene should decrease the reactivity of the olefin to dimerization and might permit the preparation of an isolable member of this class. In pursuit of this goal Berson and Salinaro prepared three *tert*-butyl-substituted derivatives of **165**. Generation of 2-*tert*-butylbicyclo[3.1.0]-hex-1(2)-ene (**192**) from ketone **193**, dimethyl (diazomethyl)phosphonate (**194**), and potassium *tert*-butoxide resulted in the isolation of recovered **193** (45%), dimeric hydrocarbon **195** (45%), and other minor products (Scheme 37).[105] The single *tert*-butyl group at C_2 does not suffice to suppress dimerization of **192**.

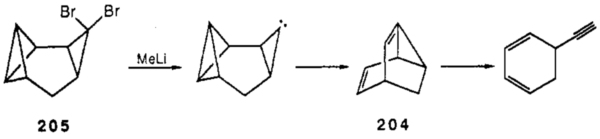
The incorporation of a second *tert*-butyl group, as in **196**, would be expected to decrease the dimerization rate. Indeed, treatment of ketone **197** with dimethyl (diazomethyl)phosphonate (**194**) and *n*-butyllithium gave a 63% yield of a mixture of monomeric hydrocarbons in addition to ca. 20% of recovered ketone **197** (Scheme 38).[105] The major component of the hydrocarbon product was cyclopentadiene **198**. Although the mechanism for this rearrangement is uncertain, a hydrogen-shift reaction, occurring at or below 20 °C, would seem to provide an escape route for bicyclo-[3.1.0]hex-1(2)-ene **196**. The result suggests that even when dimerization is sterically retarded, these unstable species can make use of normally inaccessible pathways in order to evade the bicyclo[3.1.0]hex-1(2)-ene structure.

The substitution pattern in 2-*tert*-butyl-6,6-dimethylbicyclo[3.1.0]hex-1(2)-ene (**199**) should be unfavorable to the modes of dimerization previously illustrated for other bicyclo[3.1.0]hex-1(2)-enes because both the weak σ bond (C_5–C_6) and the twisted π bond (C_1–C_2) are sterically shielded. Cleavage of the C_5–C_6 bond in **199**, however, should be more facile than in **192**. This is the case, for when **199** is generated from ketone **200** and compound **194** followed by quenching with aqueous NH_4Cl, monomeric hydrocarbons **201** and **202** are isolated. Bicyclo[2.1.0]pentane **203** is isolated in 63% yield if the acid workup is omitted (Scheme 39).[106] In neither instance is any dimeric product observed. Although extremely sensitive to atmospheric oxygen, in degassed solution **203** has proven to be the most stable member of the bicyclo[2.1.0]pentane series yet prepared.

SCHEME 39



The incongruous-like compound **204**, a highly strained bicyclo[3.1.0]hex-1(2)-ene derivative, was postulated as an intermediate in the methyllithium-induced conversion of dibromide **205** to 5-ethynyl-1,3-cyclohexadiene.[107]



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