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CYCLOPROPARENES

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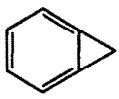
1. INTRODUCTION

Benzocyclopropene **1**[1] and its derivatives and homologs are the most highly strained members of the class of 1,2-bridged aromatic hydrocarbons. The unexpected stability and the expectation that unusual chemical and physical properties might result from the disruption of the aromatic sextet have led to the synthesis of a large number of these compounds. The purpose of this report is to provide a review of earlier work and describe recent advances in the field.[4]

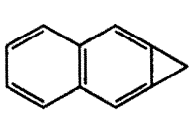
2. NOMENCLATURE

As a class, these 1,2-bridged bicyclic systems are referred to as benzocyclopropenes or cycloproparenes. Individual compounds are generally named under 'fusion nomenclature' using the cyclopropa-prefix (IUPAC Rule A 213) for systems of at least two rings of five or more members. Thus **1** must be named bicyclo[4.1.0]hepta-1,3,5-triene and not as 1H-cyclopropabenzene under the IUPAC system.

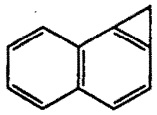


1
bicyclo[4.1.0]hepta-1,3,5-triene
benzocyclopropene

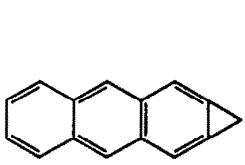
The naphthalene derivatives, however, can be named as 1H-cyclopropa[b]naphthalene and 1H-cyclopropa[a]naphthalene. Other homologs are named similarly (1H-cycloprop[b]anthracene, 1H-cyclopropa[b]phenanthrene, etc.).



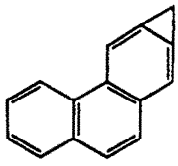
1H-cyclopropa[b]naphthalene
naphtho[b]cyclopropene



1H-cyclopropa[a]naphthalene
naphtho[a]cyclopropene



1H-cycloprop[b]anthracene
cycloprop[b]anthracene

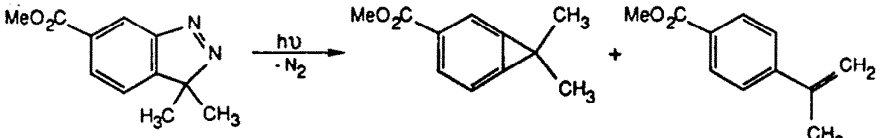


1H-cyclopropa[b]phenanthrene
cyclopropa[b]phenanthrene

The lower homologs have also been named as cyclopropene derivatives, and **1** becomes benzocyclopropene. Similarly, cyclopropa[b]naphthalene and cyclopropa[a]naphthalene can be named as naphtho[b]cyclopropene and naphtho[a]cyclopropene, respectively. Use of this system brings benzocyclopropene more in line with the other benzocycloalkenes, and is perhaps more descriptive of the compound's character than bicyclo[4.1.0]hepta-1,3,5-triene. In this report we will use the formal nomenclature except for the parent compound which will be named benzocyclopropene.

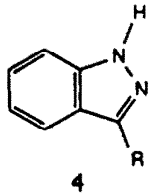
3. SYNTHESIS

The first synthesis of a cycloproparene was in 1964 with the isolation of **2** by Anet and Anet.[5,6] The 3H-indazole **3** was found to eliminate molecular nitrogen upon photolysis with the formation of **2** in low yield. This route has been employed successfully by Closs[7] in the synthesis of *gem*-



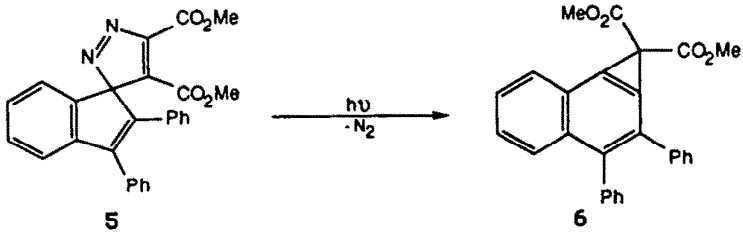
3 **2**

disubstituted cycloproparenes; however, the method cannot be applied to the synthesis of monosubstituted cycloproparenes since the indazole tautomerizes readily to the 1H form **4**.

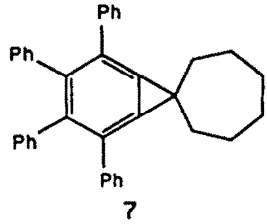


4

A substituted cyclopropanaphthalene was prepared by Dürr and Schrader[8] utilizing spiro-3H-pyrazole **5**. Irradiation of **5** gave the cyclopropa[a]napthalene **6**. A similar approach led to the synthesis of the novel spirobenzocyclopropene **7**.[9]



5 **6**



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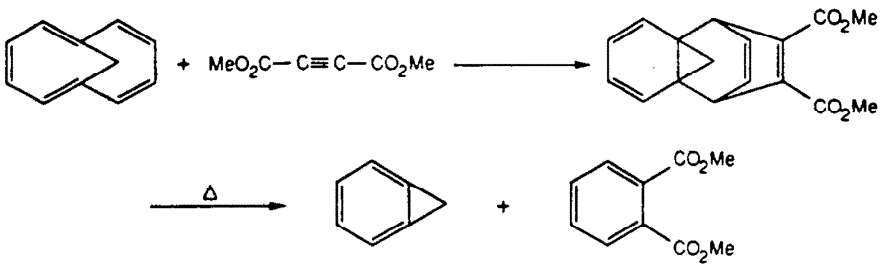
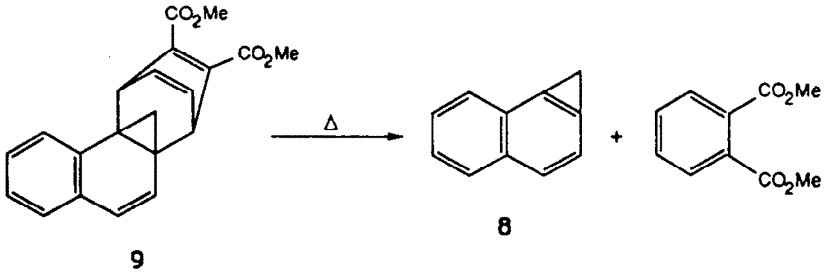
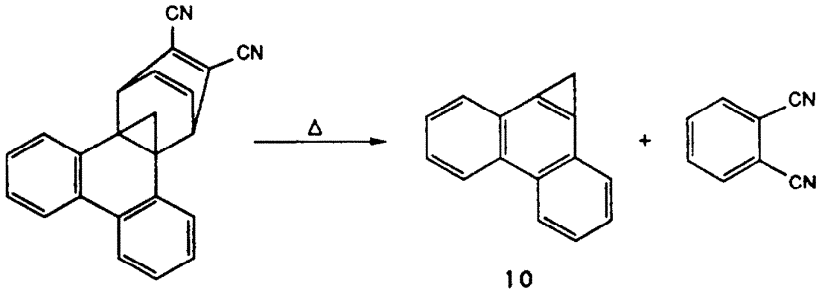


Scheme I[10].

A non-photochemical route to cycloproparenes (Scheme I) was developed by Vogel in 1963 and used to synthesize benzocyclopropene.[10] This elegant route, which uses 1,6-methano[10]annulene as a point of departure, has also been used to synthesize 1H-cyclopropa[a]naphthalene **8** by the pyrolysis of **9**.[11] More recently, 1H-cyclopropa[l]phenanthrene **10** has yielded to synthesis via this scheme.[12] Both **8** and **10** are unstable at room temperature, perhaps reflecting the formally enhanced olefinic character of the bridging double bond.



9 **8**



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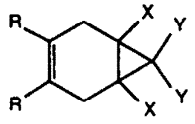
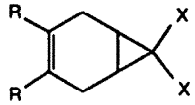
One of the more exploited routes to cycloproparenes uses halogenated bicyclo[4.1.0]heptane derivatives such as **11** and **12**. In one approach the bicycloheptane is prepared by the Diels–Alder



X = Br, Cl
Y = Cl, F

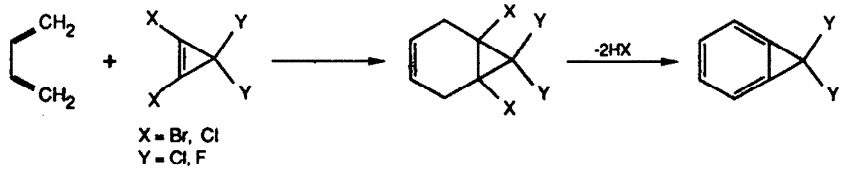
11



X = Br, Cl

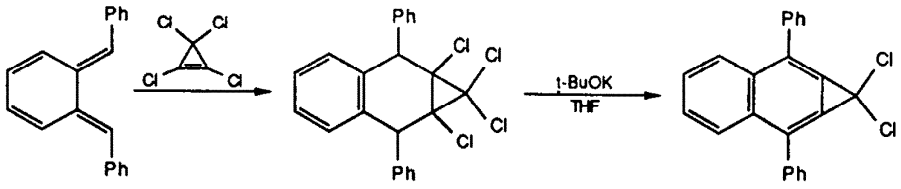
12

addition of 1,3-dienes to tetrahalocyclopropenes. Dehydrohalogenation of the Diels–Alder adduct gives the 7,7-dihalobenzocyclopropene,[13] as illustrated in Scheme II.



X = Br, Cl
Y = Cl, F

Scheme II[13].



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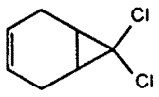
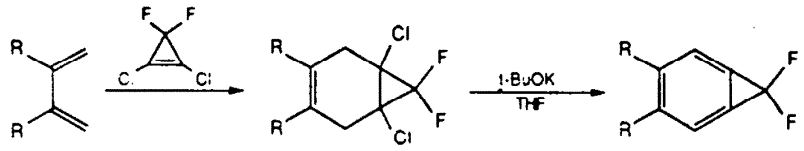


14

15

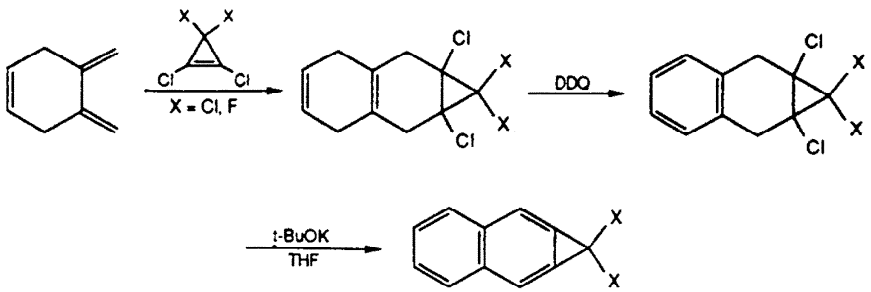
The tetrahalogenocyclopropene route has found wide application in the synthesis of dihalocycloproparenes as exemplified in the synthesis of **13**.[14] Several additional examples[15–18] are illustrated without comment in Schemes III–VI.

Halogenated bicyclo[4.1.0]heptenes, such as **12**, can be prepared by the addition of dihalocarbenes to a cyclohexadiene or a benzoannelated cyclohexadiene. Benzocyclopropene itself can be synthesized on a preparative scale from either 7,7-dichlorobicyclo[4.1.0]hept-3-ene **14**[19,20] or the isomer **15**. The generally accepted mechanism of this reaction for the more commonly used precursor **14** is

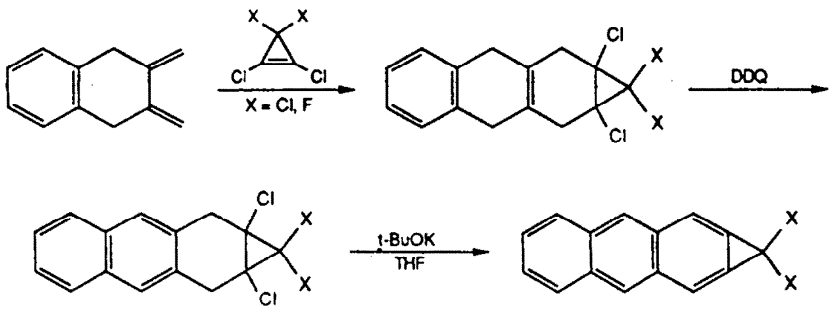


R = Me, Ph, -$(CH_2)_2$-, -$(CH_2)_3$-, -$(CH_2)_4$-

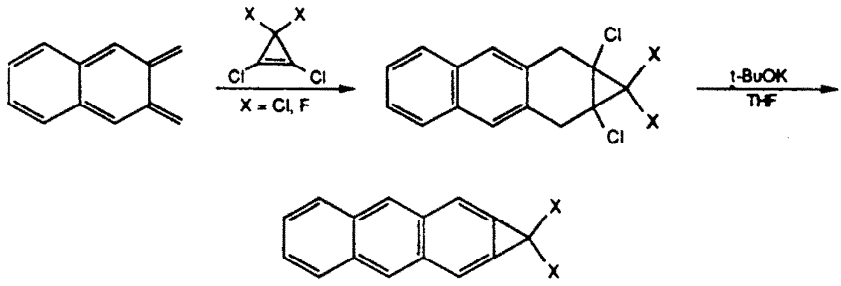
Scheme III[15].



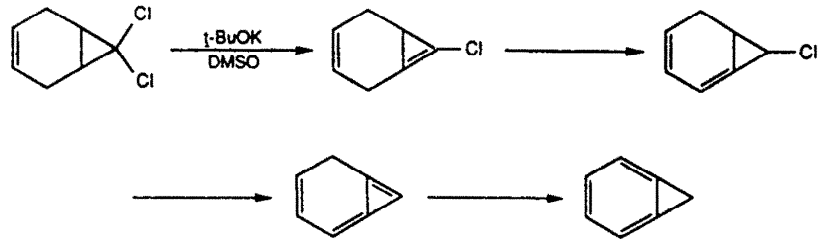
Scheme IV[16].



Scheme V[17].



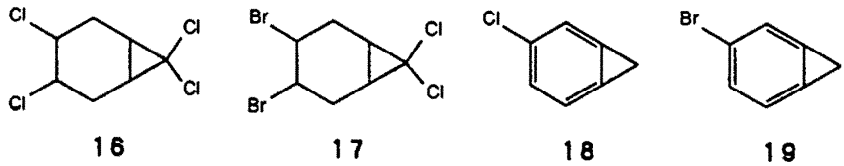
Scheme VI[18].



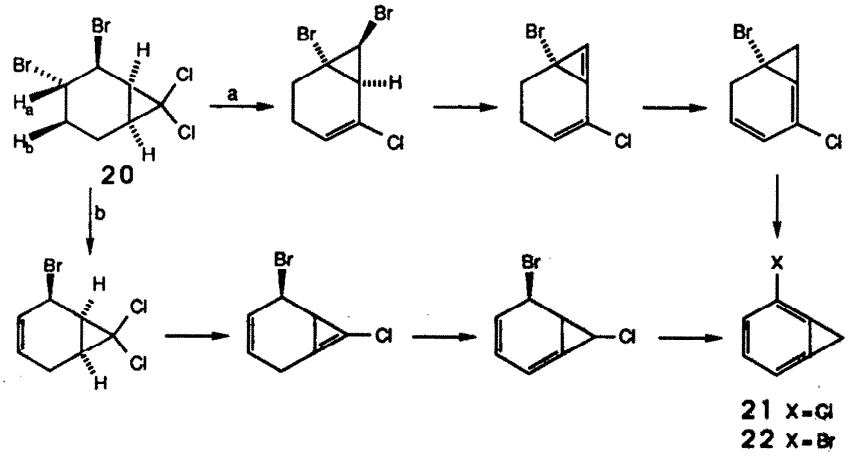
Scheme VII[19,20]

illustrated in Scheme VII.[20a] Simple benzocyclopropenes such as 2- and 3-methylbenzocyclopropene can also be prepared via this route.[21]

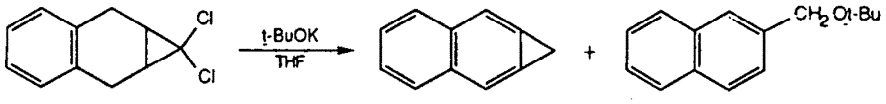
Unsaturation in the bicyclic precursor is not necessary when appropriate leaving groups are present. Thus tetrahalobicyclohexanes **16** and **17** afforded the respective 3-halobenzocyclopropenes **18** and **19**.[22,23] An earlier report which placed the halogen in **18** and **19** at C_2 is incorrect;[24] however,



when **20** was subjected to the dehydrohalogenation reaction, the major product was found to result from a skeletal rearrangement, giving benzocyclopropene **21** (path a) along with **22**[25] (path b). These observations are summarized in Scheme VIII.



Scheme VIII[25].

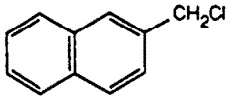


24 23 25

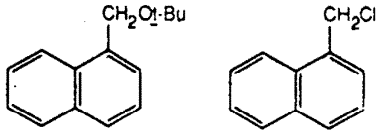
1H-Cyclopropa[b]naphthalene **23** can be prepared in 65% yield as a rather stable crystalline solid from the benzo derivative **24**.[26] A small amount of the *t*-butyl ether **25** is thought to be derived from the chloride **26**, an isolable product under different reaction conditions.

The solvent-base combination used for this reaction is particularly important. Whereas benzocyclopropene can be prepared from **14** (or **15**) using potassium *t*-butoxide in dimethyl sulfoxide, the synthesis of **23** requires a high concentration of potassium *t*-butoxide in tetrahydrofuran for a satisfactory yield. The yield of **23** from the potassium *t*-butoxide–dimethyl sulfoxide combination is $< 10\%$.

Browne and Halton[27] have reassigned the β-substituted naphthalenes **25** and **26** as the α-isomers **27** and **28** and proposed an unprecedented intramolecular S_N2 displacement on the cyclopropane to account for the skeletal rearrangement. We have also observed these products, but have traced their origin to an impurity(ies) in the starting material; otherwise, none of the rearranged product is produced.[28]

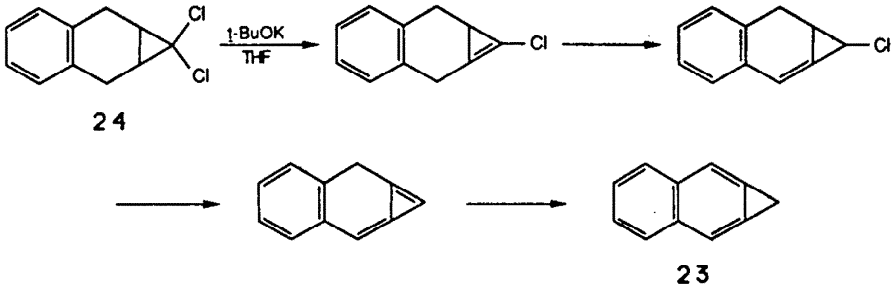


26



27 28

The observation that a high concentration of potassium *t*-butoxide is required for the transformation **24** → **23** suggests that an aggregate of *t*-butoxide (high kinetic order) is required to effect the deprotonation leading to **23**. In this regard, *t*-butoxide is known to exist as a tetramer in tetrahydrofuran.[29] Subsequent steps in this reaction would be strictly analogous to those described earlier in Scheme VII.

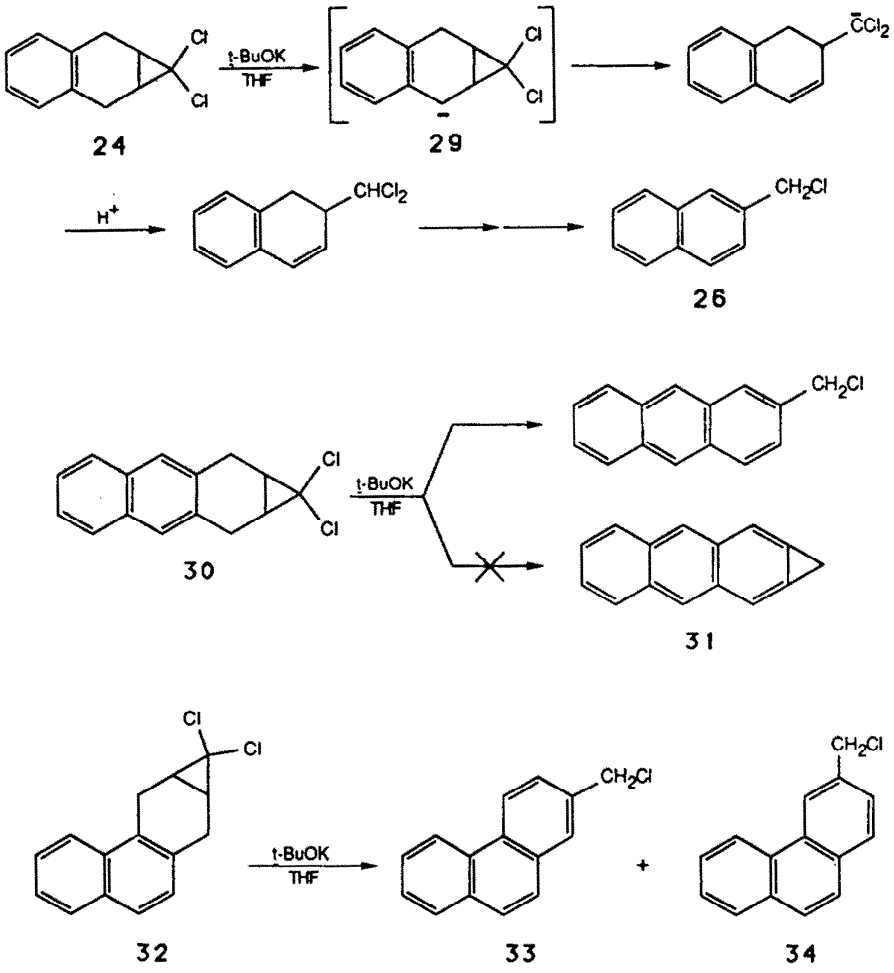


24

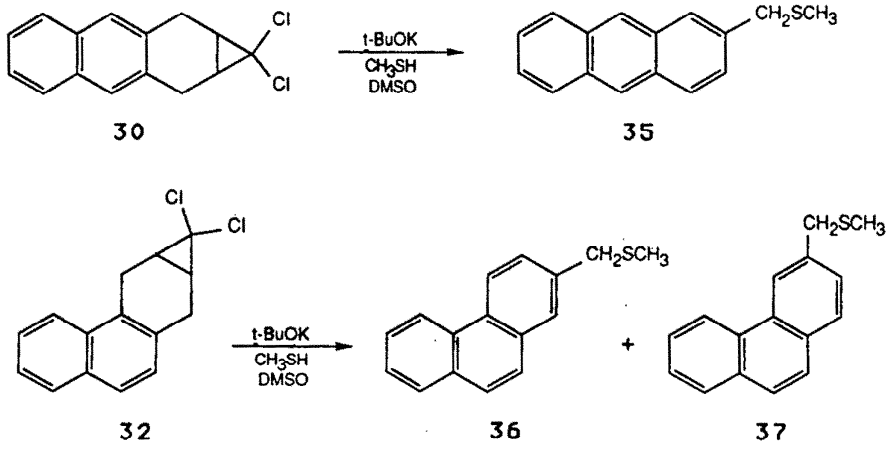
23

A competing process accounting for **25** and **26** would involve deprotonation at the benzylic carbon. This would yield the cyclopropylcarbinyl anion **29** which upon rearrangement to the homoallylic anion could be transformed readily into **26**.

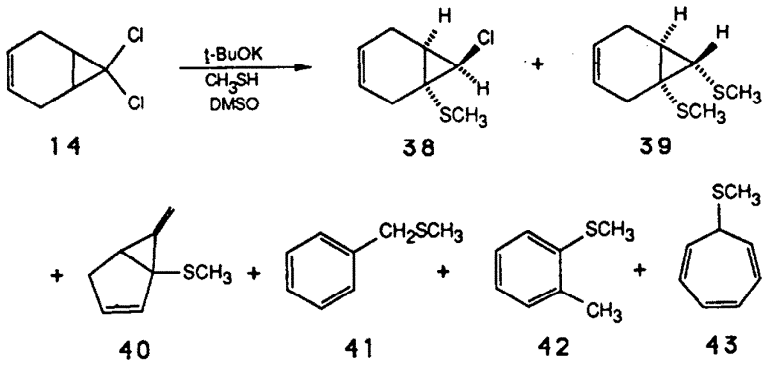
This pathway might become even more important with compounds such as **30**, since the anion would be expected to experience greater resonance stabilization by the aromatic pendant (naphthalene *vs.* benzene). Consistent with this hypothesis is the observation that **30** yields 2-substituted anthracenes.[30] None of the expected cycloproparene **31** could be isolated. Similar observations were made when **32** was treated with potassium *t*-butoxide in tetrahydrofuran. The chlorides **33** and **34** were isolated in $> 90\%$ combined yield.[28]



Trapping experiments using methyl mercaptide to test for cyclopropene intermediates are in agreement with these conclusions.[31] For example, treatment of **30** with potassium *t*-butoxide in dimethyl sulfoxide containing methyl mercaptide afforded sulfide **35** in 94% yield, whereas **32** afforded a quantitative yield of the isomeric 2- and 3-(thiomethyl)methylphenanthrenes **36** and **37**,[28] via the chlorides **33** and **34**.



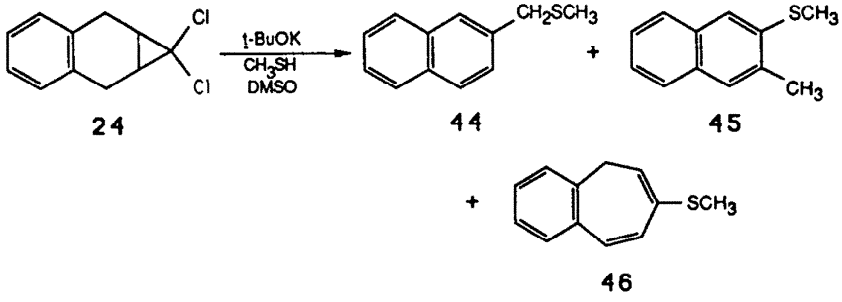
In contrast, compound **14**, which can be converted readily into benzocyclopropene under the conditions used for the trapping experiment, yields cyclopropene derived products **38** and **39** along with four additional products provisionally identified as **40–43**. As expected, the product ratios are strongly dependent on reaction time. After 1 h the yield of **38** is 42%, but only 5% after 2.5 h.



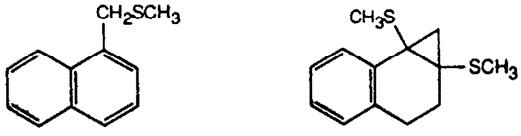
14 38 39

40 41 42 43

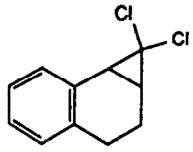
The reaction of **24** (pure by NMR, TLC, GC/MS) afforded **44** as the major product along with **45** and **46** (*ca* 6% combined yield). The absence of cyclopropyl sulfides is not surprising since the reaction does not yield cyclopropa[b]naphthalene efficiently under the reaction conditions. Compounds **47** and **48** were observed when the starting material was not purified carefully. The observation that compound **48** can also be derived from **49** suggests that **49** might be a precursor to the rearranged products **27** and **28** observed by Halton and his co-workers.[27]



24 44 45 46

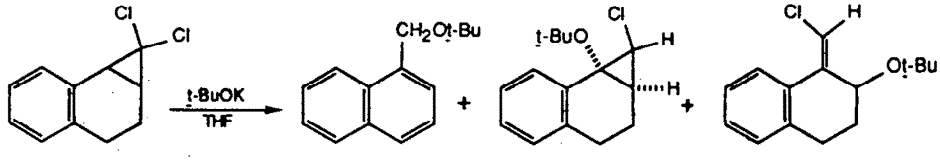


47 48

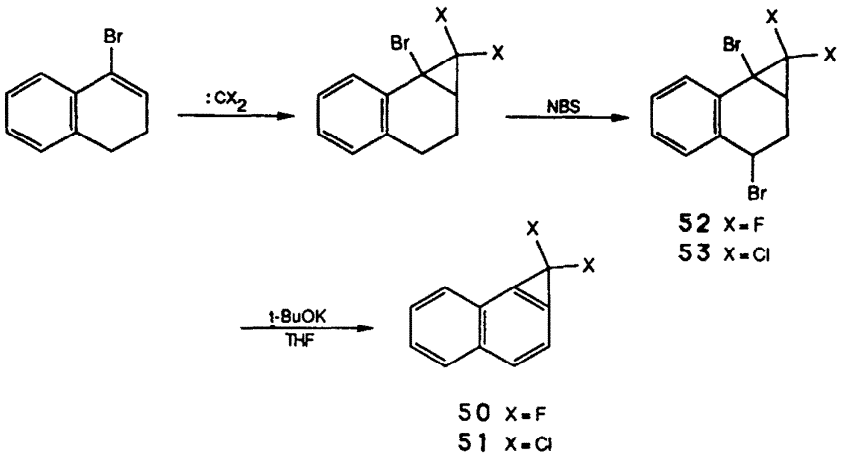


49

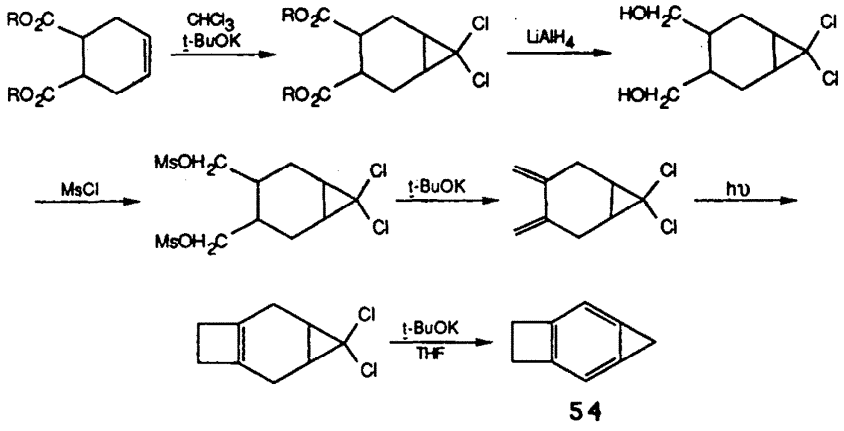
Nonlinearly fused cyclopropareneS such as cyclopropa[a]naphthalene are inaccessible via the *gem*-dichlorocyclopropane route, since isomerization of the initially produced cyclopropenyl double bond requires disruption of a benzene ring, and other reactions are preferred as illusrated in the case of **49**;[31] however, the very reactive 1,1-dihalogeno-1H-cyclopropa[a]naphthalenes **50** and **51** can be prepared[32] by dehydrobromination of the appropriate brominated carbene adducts (**52** and **53**, respectively) of 4-bromo-1,2-dihydronaphthalene (Scheme IX).



49

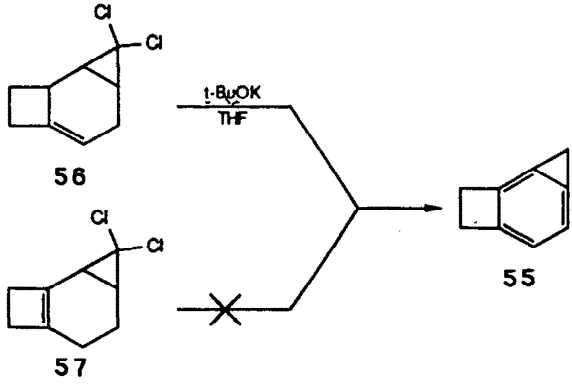


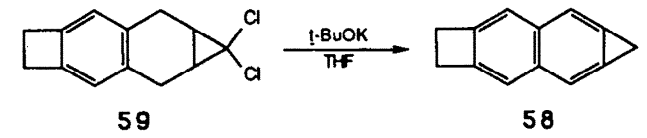
Scheme IX[32].



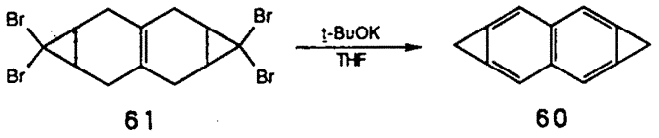
Scheme X[33].

Despite these limitations, this method has been applied to the synthesis of a rather wide variety of benzocyclopropenes and their naphtho analogs. Both compounds in which benzene is fused to a three- and a four-membered ring have been reported by Davalian and Garratt.[33] The linear isomer **54** was prepared via the route outlined in Scheme X, whereas the isomer **55** could be derived from **56**. The analogous route from **57** fails, however, since the tetrasubstituted double-bond cannot be induced to migrate from the four-membered ring as would be required by the mechanism of Scheme VII.





59 58



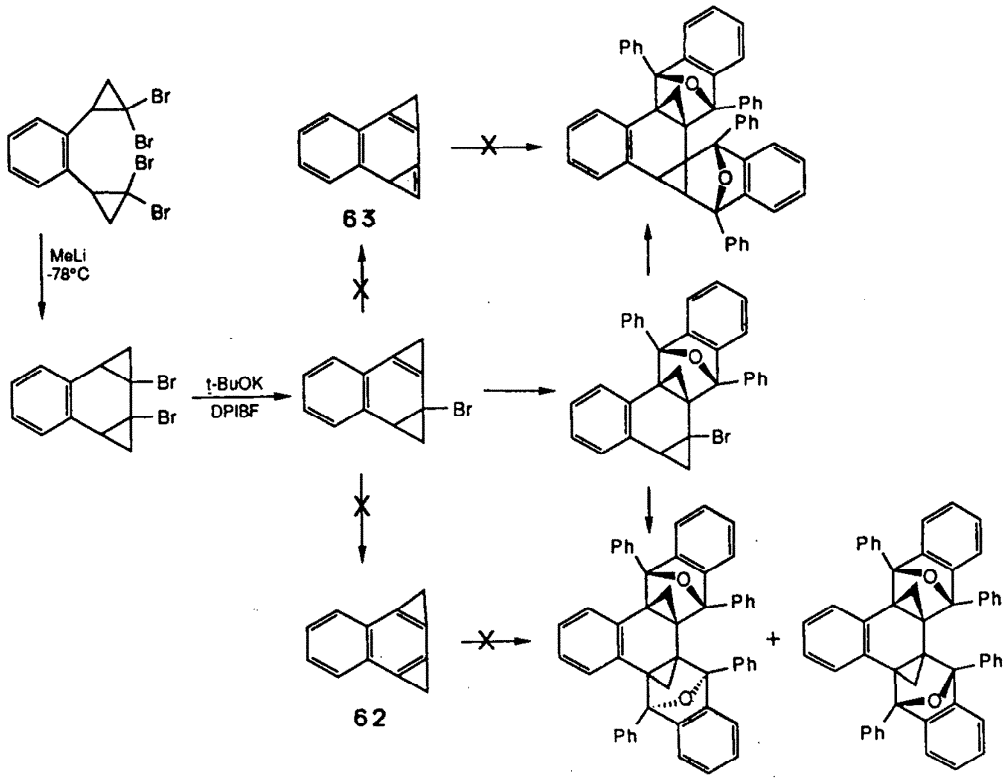
61 60

The highly reactive naphthalene **58** can be prepared readily from **59**.[33] An even more strained naphthalene, compound **60**, has been prepared from **61**.[34] The high strain energy of this compound is manifested by a tendency to explode upon melting.

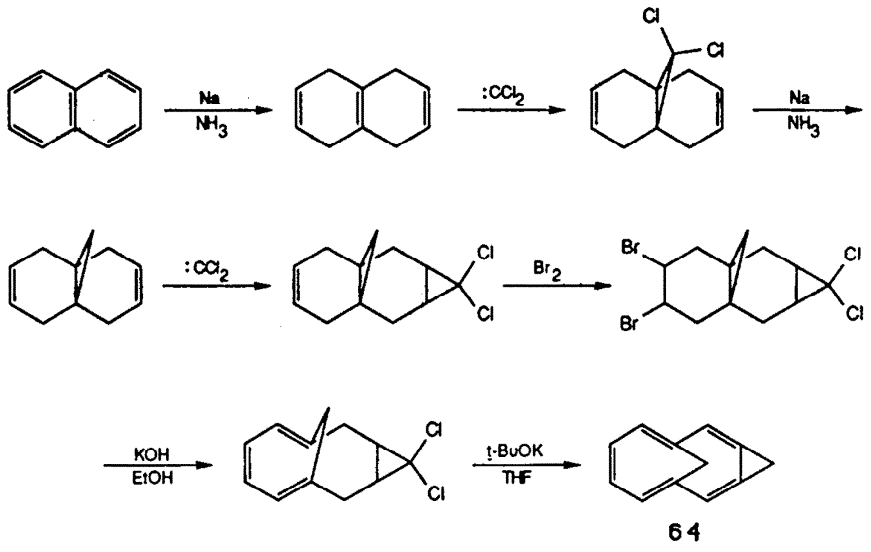
Recently the formal Diels–Alder adducts of dicyclopropa[a,c]naphthalene **62** and its isomer **63** with 1,3-diphenylisobenzofuran have been isolated (Scheme XI).[35] Evidence indicates that stepwise 1,2-eliminations and additions of 1,3-diphenylisobenzofuran take place.

Fusion of Vogel's 1,6-methano[10]annulene to cyclopropene leads to the interesting compound **64** (Scheme XII). This compound is much less stable than benzocyclopropene or the isoelectronic cyclopropa[b]naphthalene and tends to polymerize at room temperature.[36] Compound **64** has achieved reagent status in the Cologne laboratory as several kilograms have been synthesized.

1,1-Dichlorocyclopropa[l]phenanthrene **65** is thought to be an intermediate in the elimination of phenylselenic acid from **66**.[37] Formation of **65** is based on the reaction of the selenoxide elimination product with methanol to give the carboxylate. Analogous reactions of 1,1-dihalocycloproparenes with alcohols are well known.[32,38] Attempts to trap **65** with dienes have failed.

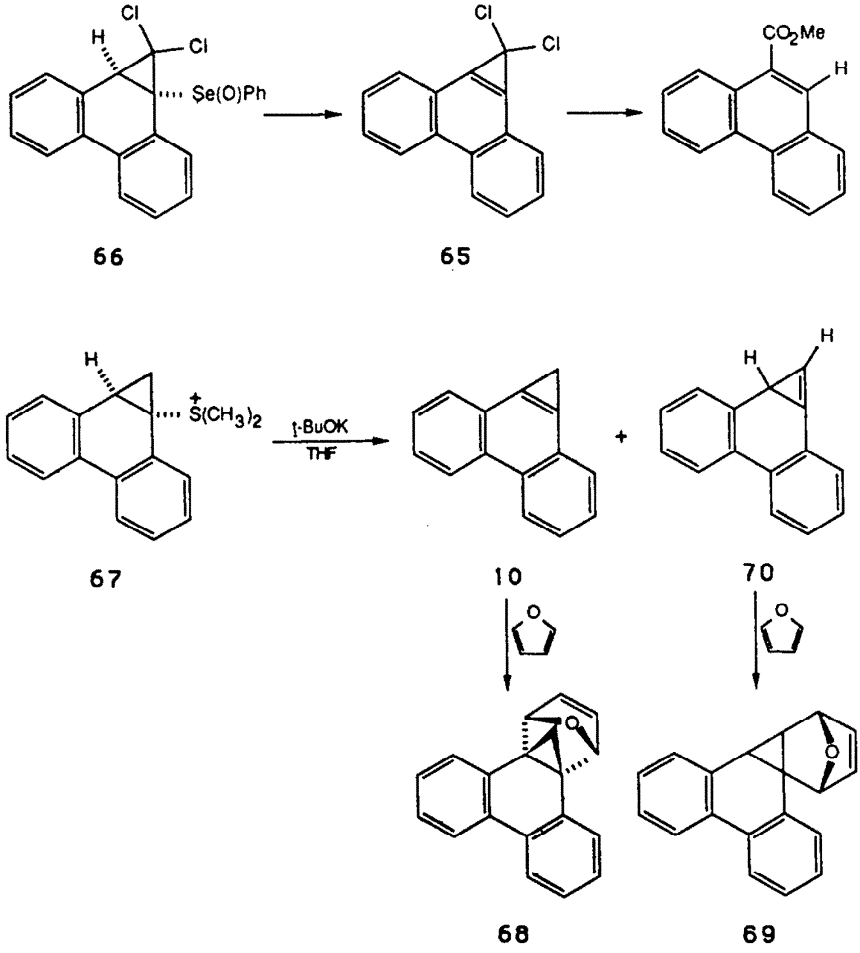


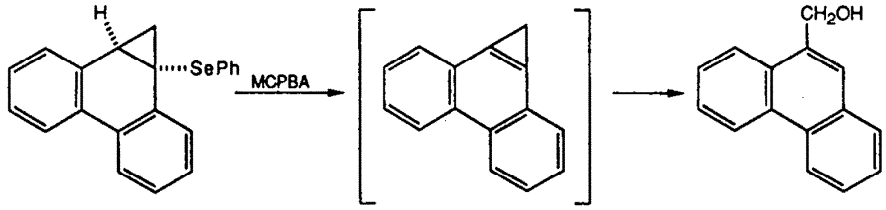
Scheme XI[35].



Scheme XII[36].

Base-induced elimination of the sulfonium salt **67** in the presence of furan affords the addition products **68** and **69**, derived from 1H-cyclopropa[l]phenanthrene **10** and the isomeric cyclopropene **70**.[39] Upon oxidation, the selenide **71** yields phenanthrene-9-methanol, presumably via **10**.[39] No evidence for the intermediacy of **10** is obtained from the sulfoxide pyrolysis of **72**,[39] which leads to products formed by radical pathways (Scheme XIII).

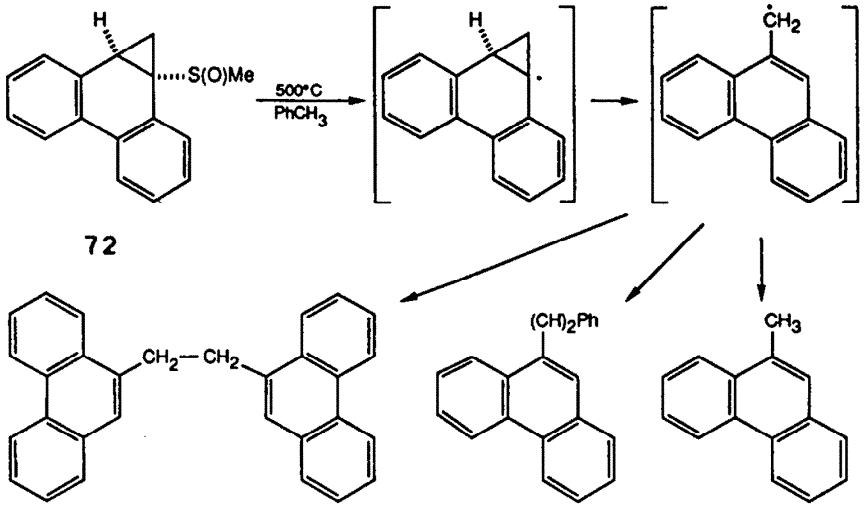




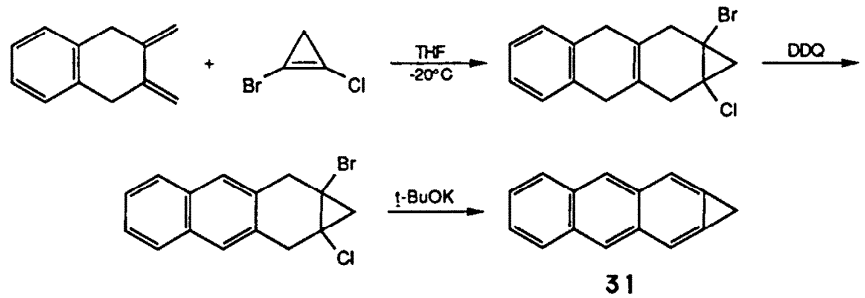
71 10

The introduction of 1-bromo-2-chlorocyclopropene as a synthon represents a major advance in the synthesis of cyclopropparenes. The anthracene **31**, inaccessible by other routes, can be prepared readily using the cyclopropene in a key step of the synthesis (Scheme XIV).[40] Cyclopropa[b]phenanthrene **73**, one of three remaining cyclopropaphenanthrenes,[12] can be prepared via the straightforward sequence of reactions in Scheme XV.[41]

1-Bromo-2-chlorocyclopropene has also been used in the facile syntheses of several bis- and tris-annelated benzenes which incorporate the three-membered ring. A two-step synthesis of **74** is illustrated below.[42] Compound **74** is probably the most strained cyclopropparene, yet it possesses remarkable kinetic stability; a solution of **74** in $CDCl_3$ decomposes only after 36 h at room temperature. The tris-annelated compounds **75** and **76** have also been prepared from the corresponding dienes and the cyclopropene.

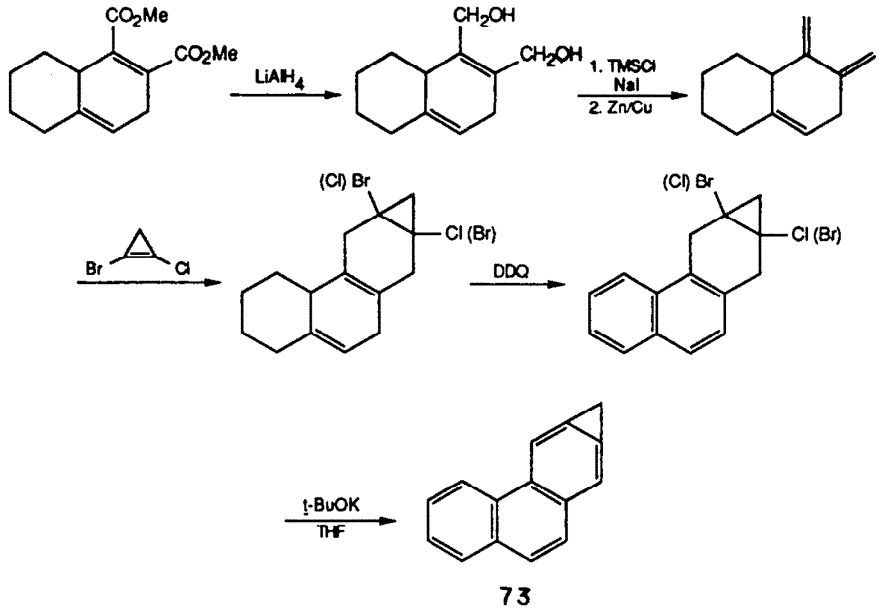


Scheme XIII[39].



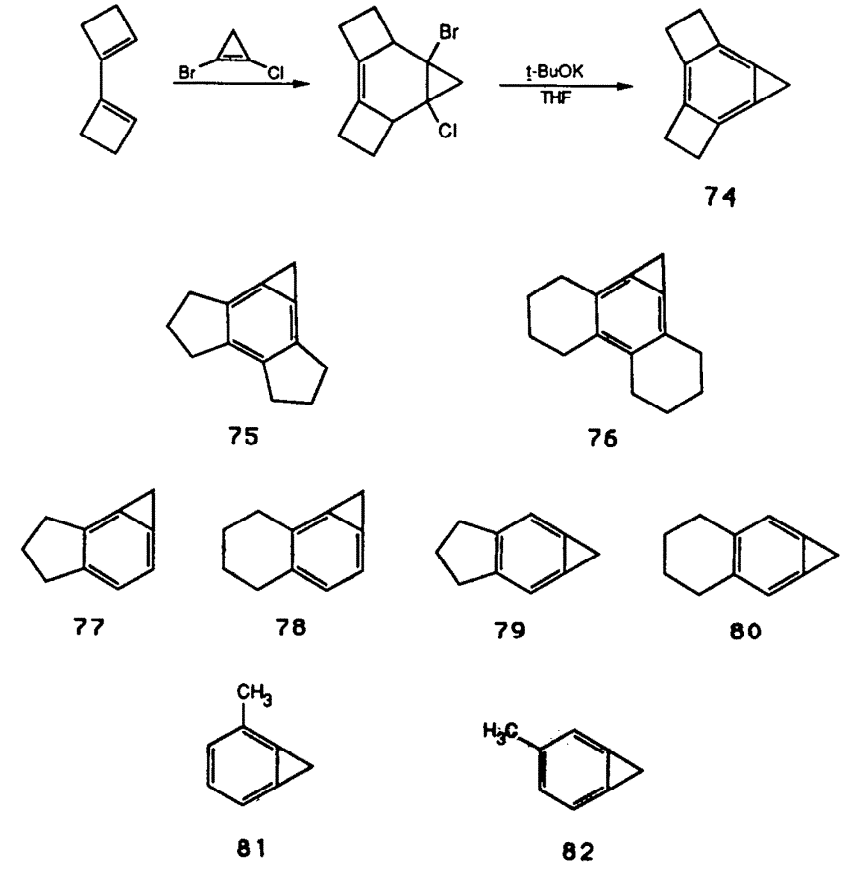
31

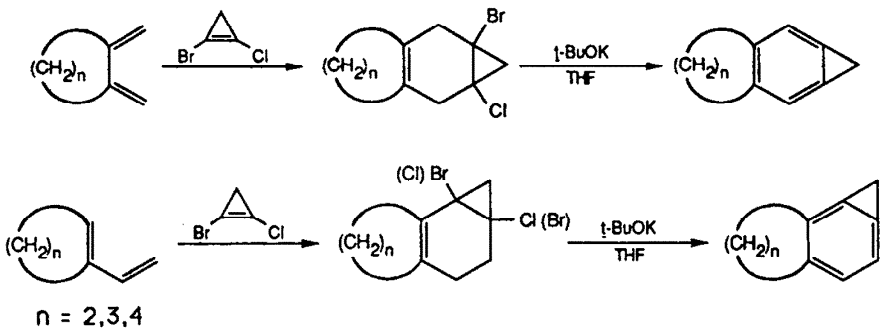
Scheme XIV[40].



Scheme XV[41].

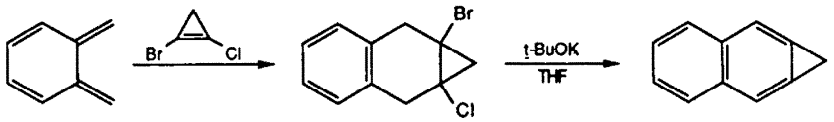
Reactions of 1-vinylcycloalkenes and 1,2-dimethylenecycloalkanes with 1-bromo-2-chlorocyclopropene have been used to produce precursors to several bis-annelated benzenes, thus providing a convenient route to linearly and nonlinearly fused benzocyclopropenes.[43] Compounds **77–80**, as well as **54** and **55**, can be prepared readily using the procedure outlined in Scheme XVI. Compounds **81** and **82** have also been prepared via the Diels–Alder route using the appropriate acyclic dienes and 1-bromo-2-chlorocyclopropene.





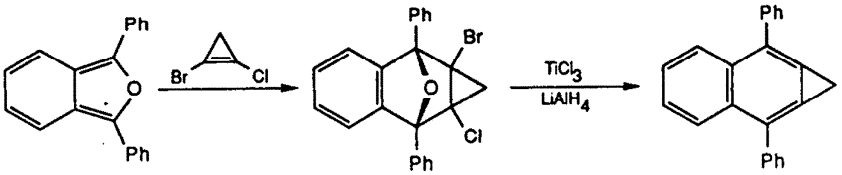
Scheme XVI[43].

Other recent applications include the syntheses of **23** and methyl or dimethyl derivatives by interception of appropriately substituted *o*-quinodimethanes with the cyclopropene and subsequent dehydrohalogenation of the adducts.[44]



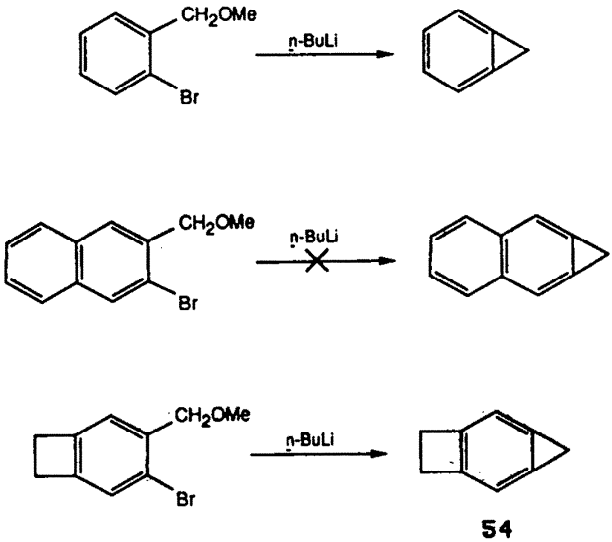
23

A further interesting example[45] is the synthesis of 2,7-diphenyl-1H-cyclopropa[b]naphthalene **83** via cycloaddition of 1,3-diphenylisobenzofuran to 1-bromo-2-chlorocyclopropene followed by aromatization of the adduct with low-valent titanium.

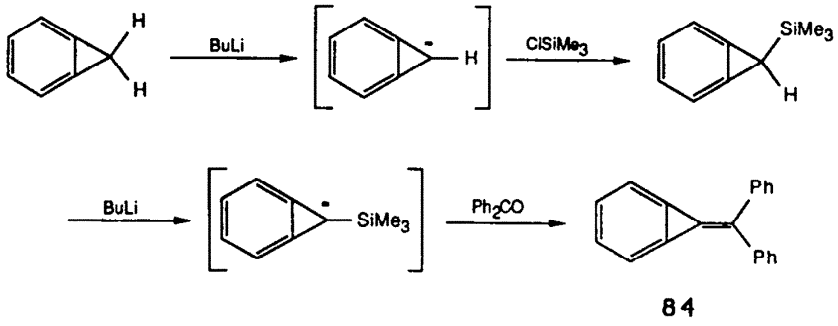


83

Benzocyclopropene has been prepared[46] by treating *o*-bromobenzyl methyl ether with butyllithium. Unfortunately, this potentially useful method fails for cyclopropa[b]naphthalene[47] and does not appear to be very general as only one other successful application of this reaction has been reported. Compound **54** can be prepared in 5% yield.[48]



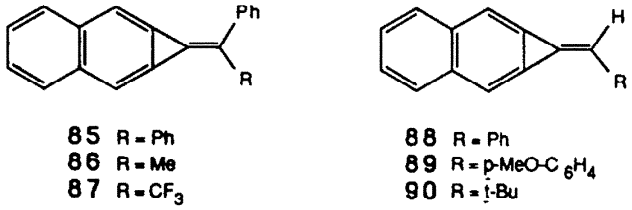
54



84

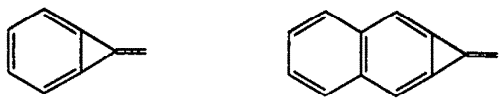
Scheme XVII[49].

1,1-Diphenylmethylenecyclopropabenzene **84**, a compound of considerable theoretical interest, has been reported recently.[49] This synthesis makes use of both the cyclopropabenzenyl anion and the Peterson olefination to obtain **84** as a stable yellow solid (Scheme XVII). Several other derivatives of methylenecyclopropabenzene as well as the 1-alkylidene-1H-cycloproparenes **85–90** derived from 1H-cyclopropa[b]naphthalene can also be synthesized using this scheme.[50] Although neither of the parent hydrocarbons (**91** or **92**) has been reported, **91** has been postulated as an intermediate in the following reaction.[51]

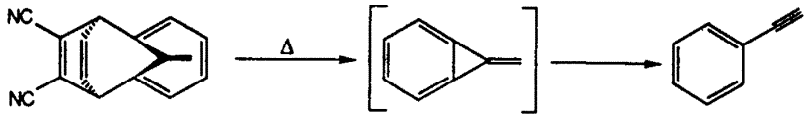


85 R = Ph
86 R = Me
87 R = CF_3

88 R = Ph
89 R = p-MeO-C_6H_4
90 R = t-Bu



91 92

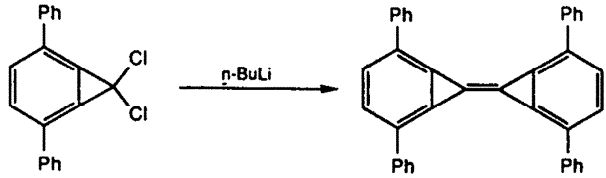


91

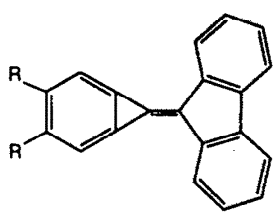
The fascinating hydrocarbon **93**, obtained by treating **94** with *n*-butyllithium, has also been reported recently.[52]

The benzocalicenes **95** and **96** and the first triaheptafulvalenes **97–100** are available by Peterson olefination of the corresponding cycloproparene with the appropriate ketone.[53]

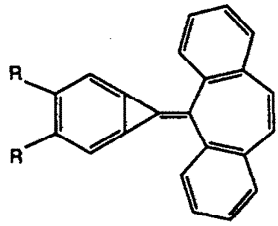
The generation and trapping of both cyclopropabenzynes **101** and **102** emphasizes the remarkable ability of the benzenoid framework to accommodate strain. These compounds can be generated and



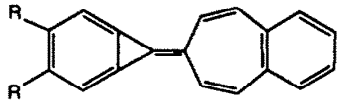
94 93



95 R = H
96 RR = benzo



97 R = H
98 RR = benzo



99 R = H
100 RR = benzo

trapped as the furan adducts **103** and **104** by treating the bromobenzocyclopropenes **19** and **21** with the complex base system of *t*-butoxide ion/amide ion (Scheme XVIII).[54] Use of the classical method of amide ion in liquid ammonia gave inconclusive results. The formation of the linear benzyne from **19** appears to be highly regioselective, since none of the nonlinear adduct is obtained. Compound **101** is calculated to be less stable than **102** by 2.5 kcal/mol.[54]

Although a single, well-conceived attempt to synthesize **105** failed,[55] the formation of the cyclopropabenzynes raises hope that **105**, **106**, or **107** might be isolable or exist as a transient intermediate.

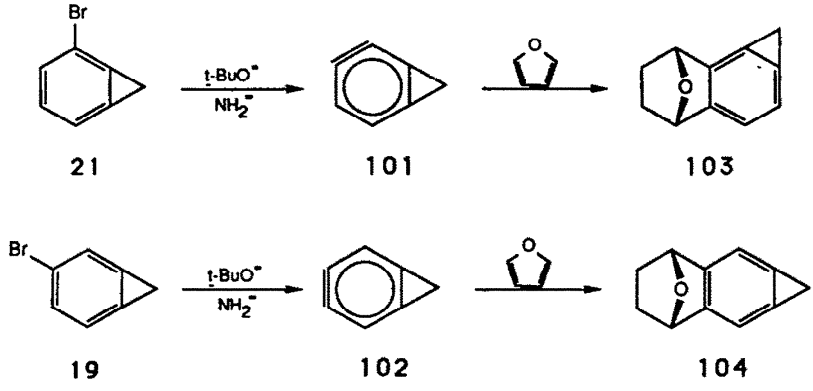
An area that has seen little activity is the synthesis of cycloproparenes containing heteroatoms. Although cyclobutapyridines are a well-known class of compounds,[56] only recently has the first cyclopropapyridine been reported; photolysis of the pyrazolopyridine **108** afforded the cyclopropapyridine **109** and an isomeric isopropenylpyridine.[57]

4. CHEMISTRY OF CYCLOPROPARENES

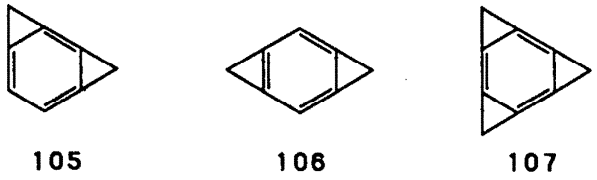
It is not surprising that the chemistry of the cycloproparenes is dominated by reactions involving cleavage of the three-membered ring, a property which prevents aromatic substitution of the type observed in benzocyclobutenes.

The thermally induced ring opening reactions of benzocyclopropenes are thought to proceed via homolysis of the single bond to give an intermediate 1,3-diradical. Thermolysis of the parent compound **1** (vapor phase, 80°C) afforded 9,10-dihydrophenanthrene, and the diradical **110** has been trapped with butadiene.[4,58]

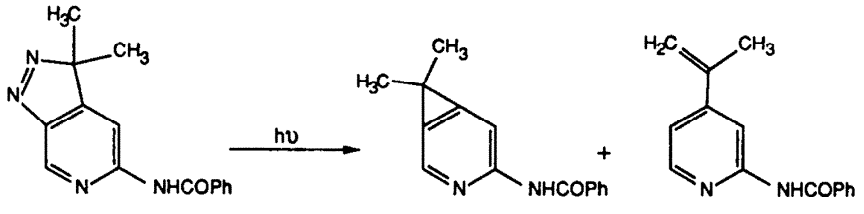
Flash pyrolysis of C_1-labelled benzocyclopropene **1**, however, affords the allene **111** as the primary product.[59] These labelling studies have shown that the ring contraction does not randomize



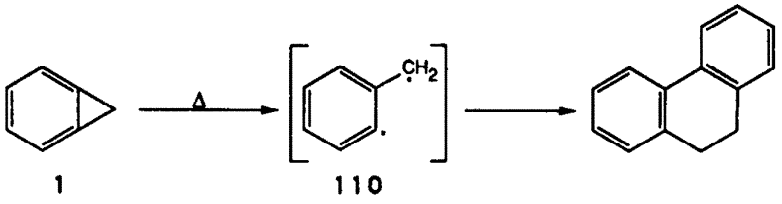
Scheme XVIII[54].



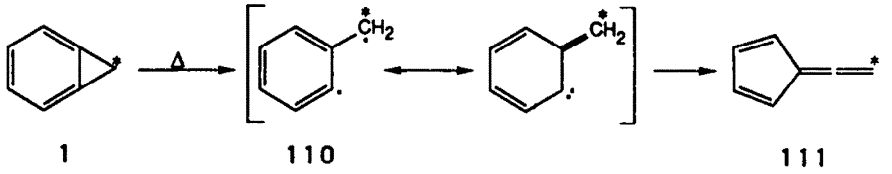
105 106 107



108 109

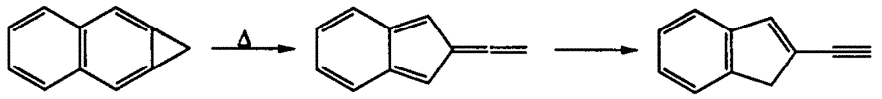


1 110



1 110 111

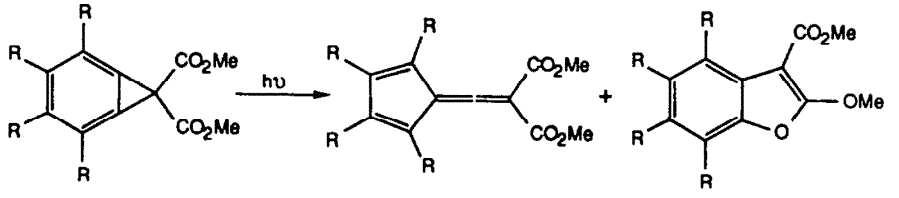
the carbon skeleton, suggesting that a Wolff-type rearrangement is implicated in this reaction. An analogous ring contraction has been observed for **23**, giving 2-ethynylinene.[60]



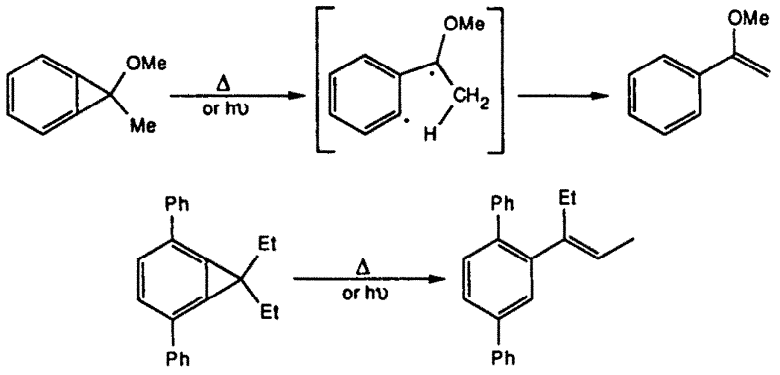
23

Diradical intermediates are also implicated in the photolysis of cycloproparenes.[61] Photolysis[62] of **112** yields the ring contracted product **113** along with the benzofuran **114**, the only product observed in the thermolysis of **112**.[8]

Cycloproparenes substituted with alkyl groups at C_7 undergo intramolecular transfer of an α-hydrogen atom both thermally and photochemically[9,62,63] through a five-membered transition state. Representative examples of these reactions are illustrated below.[64]

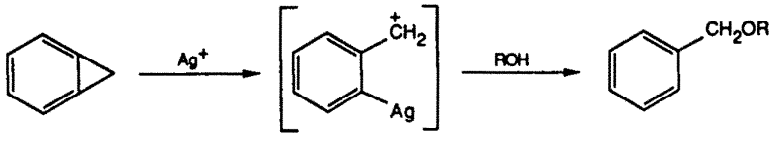


112 113 114



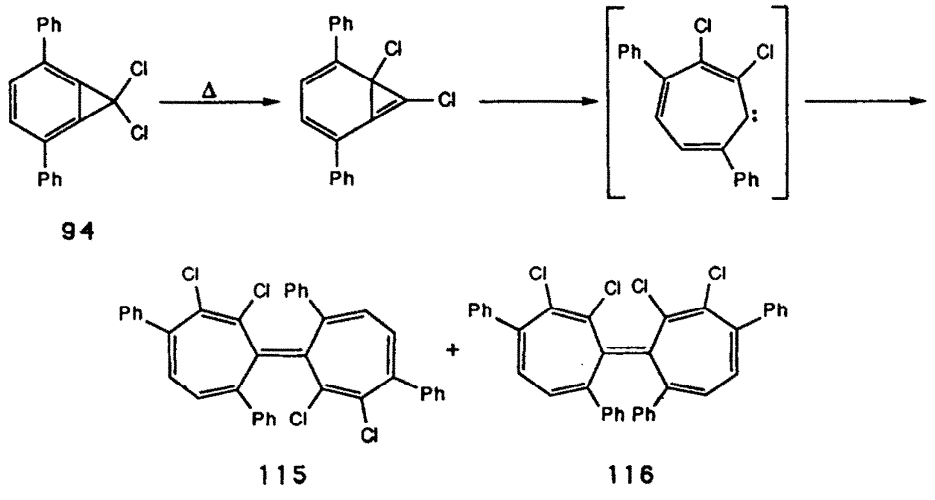
The thermolysis of 7,7-dihalocycloproparenes is quite different from the examples described above.[64,65] For instance, **94** yields the geometrical isomers **115** and **116**, identified by X-ray analysis. The formation of these dimers has been rationalized[66] in terms of the mechanism illustrated in Scheme XIX.

The three-membered ring in cycloproparenes can be cleaved readily by reaction with silver salts, yielding intermediates which can be used as excellent benzylating species. The Ag(I) catalyzed reaction of benzocyclopropene with alcohols, thiols, and amines all proceed smoothly at 0°C in aprotic solvents giving the corresponding benzylated derivatives in high yield.[67] The reaction with alcohols has been used in the characterization of several cycloproparenes.[24,34]

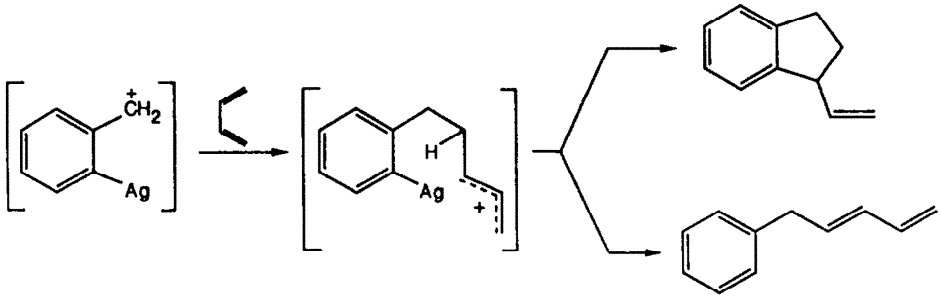


Silver ion also catalyzes the reaction of benzocyclopropene with other reagents, including alkenes, dienes, allenes, and alkynes.[68] In each case electrophilic addition of the cationic intermediate to a multiple bond yielding a new cation is observed. The resulting intermediate can then give products resulting from ring closure or proton transfer. The reaction with butadiene is illustrated in Scheme XX.

Mineral acids and halogens readily cleave the three-membered ring of benzocyclopropenes.[21,30] Reaction of **18** with hydrochloric acid yielded a mixture of 3- and 4-chlorobenzyl chloride,[22] while Ag(I) catalysis gave only the 4-chlorobenzyl ether.[23]

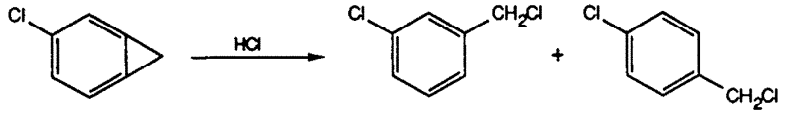


Scheme XIX[66].

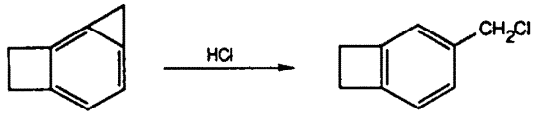


Scheme XX[68].

In contrast to the mixture obtained from **18**, reaction of the nonlinearly fused isomer **55** with HCl produced only one adduct.[69] This result seemed to indicate that the substitution pattern in

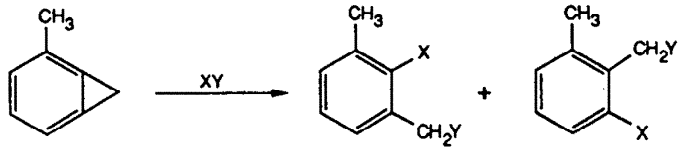


18



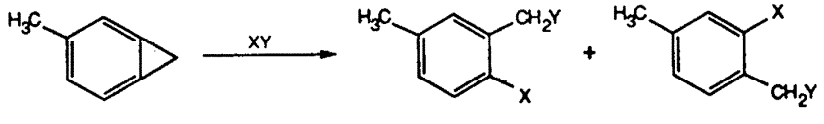
55

unsymmetrical systems might influence the regiochemistry of the ring cleavage. To test this concept, Garratt *et al.*[21] prepared several asymmetrically substituted benzocyclopropenes and reacted them with electrophiles. Compound **81** reacts with bromine, iodine, and HCl to give the *m*-xylenes **117a,b,c** as the major products, whereas it reacts with silver nitrate in the presence of ethanol and aniline to give *o*-xylenes **118d,e** as the major products. Similarly, **82** gives mainly *m*-xylenes **119a,b,c** with the halogens and HCl and gives *p*-xylenes **120d,e** with silver nitrate in ethanol or aniline. In contrast, the reaction of **55** with iodine gave **121a** predominantly, and with bromine **121b** exclusively; addition of HCl or Ag(I)-ethanol gave only **122c** and **d**. These differences in electrophilic behavior toward the two types of reagents were suggested[21] to arise from the atack of the silver ion (and the proton in the case of **55**) on the σ electrons of the cyclopropyl ring. If the reaction of **55** with silver ion proceeds via the σ route, then the observed regiochemistry would require that **123** be preferred to **124**.



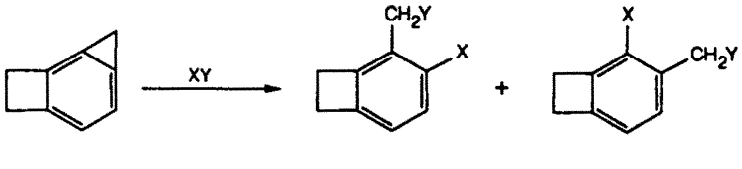
81 **117** **118**

a. X = Y = Br
b. X = Y = I
c. X = H, Y = Cl
d. X = H, Y = OEt
e. X = H, Y = NHPh



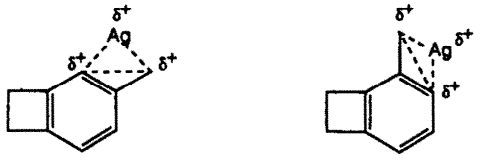
82 **119** **120**

a. X = Y = Br
b. X = Y = I
c. X = H, Y = Cl
d. X = H, Y = OEt
e. X = H, Y = NHPh



55 121 122

a. X = Y = I
b. X = Y = Br
c. X = H, Y = Cl
d. X = H, Y = OEt



123 124

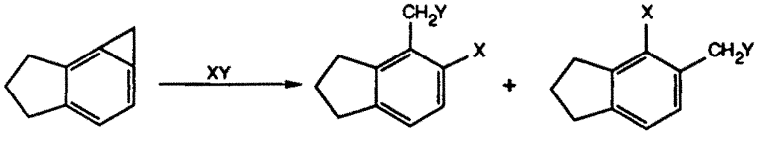
125 126

The reaction of halogens presumably proceeds by attack on the π electrons to give the intermediate in which the positive charge is adjacent to the four-membered ring, i.e. **125**, in preference to **126**.

A tendency for benzocycloalkanes with strained rings to react with electrophiles mainly β to the ring junction was first reported by Mills and Nixon[70] nearly sixty years ago. Subsequent studies by Finnegan[71] and Streitwieser *et al.*[72] on the electrophilic substitution reactions of benzocyclopropenes and biphenylene have also shown that the β position is more reactive to electrophilic substitution. Although a satisfying explanation for these results has not been presented, rehybridization of the framework which occurs in these molecules because of the bond angle requirements of the small ring is most often presented.

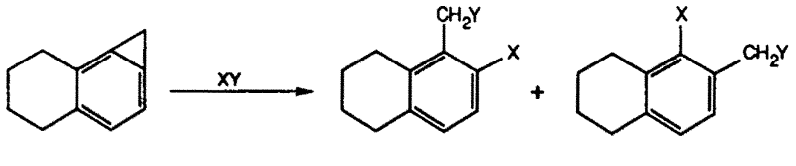
The recent availability of the annelated benzocyclopropenes **77** and **78** has resulted in a logical extension of the Garratt study.[43] The reaction of **77** with electrophiles follows a path similar to that observed by Garratt[21] for **55**. For example, the reaction with iodine gave **127a** predominantly, and with bromine gave **127b** exclusively, products resulting from cleavage of the bond β to the five-membered ring, whereas HCl and silver ion in methanol gave exclusively products derived from α-cleavage (**128c,d**). In contrast to **77**, benzocyclopropene **78** was found to react with electrophiles to yield, in each instance, both regioisomers **129** and **130**.

These results support the argument[73] that the strain resulting from fusion of a five-membered ring (**77**) leads to regiospecific cleavage of the cyclopropene; however, fusion of a six-membered ring (**78**) does not impart additional strain and thus the regioselectivity observed for **55** and **77** is lost.



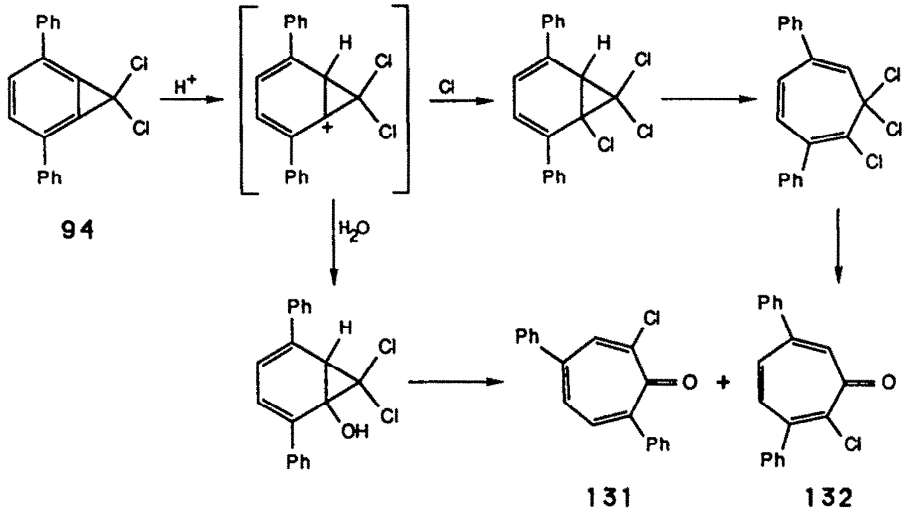
77 127 128

a. X = Y = I
b. X = Y = Br
c. X = H, Y = Cl
d. X = H, Y = OMe

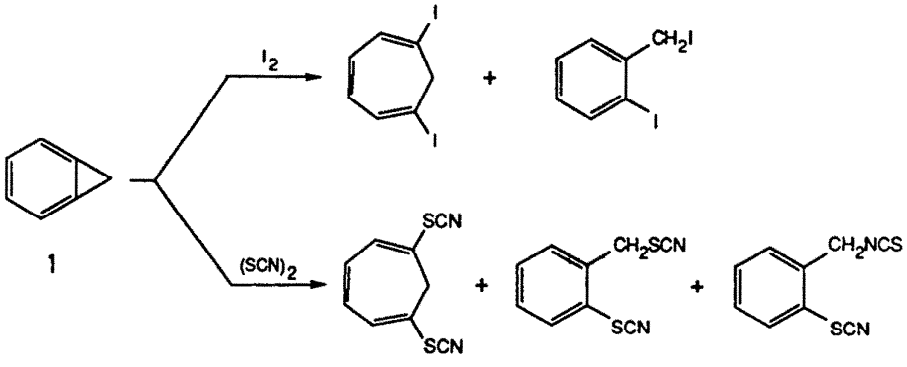


a. X = Y = I
b. X = Y = Br
c. X = H, Y = Cl
d. X = H, Y = OMe

The *gem*-dichloro derivative **94** decomposes readily in chloroform or dichloromethane to give the dimer **115** and the tropones **131** and **132**.[74] If the solvent is saturated with HCl, dimerization becomes less important, but the two tropones are still obtained. Formation of the tropone has been attributed to electrophilic attack at the bridging bond, followed by the reaction of the carbonium ion with either chloride or water.

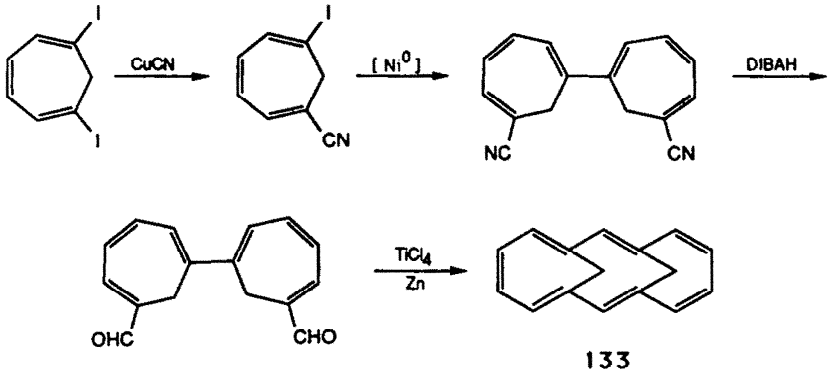


It has been noted that, in the reaction of **1** with iodine, small quantities of 1,6-diiodocycloheptatriene accompany the major product, *o*-iodobenzyl iodide.[4,58] This product has been shown to result from a photochemical reaction, and with photolysis at >400 nm the cycloheptatriene becomes the major product. Benzocyclopropene also produces a cycloheptatriene when photolyzed with thiocyanogen.[75] These functionalized cycloheptatrienes have been converted to other important

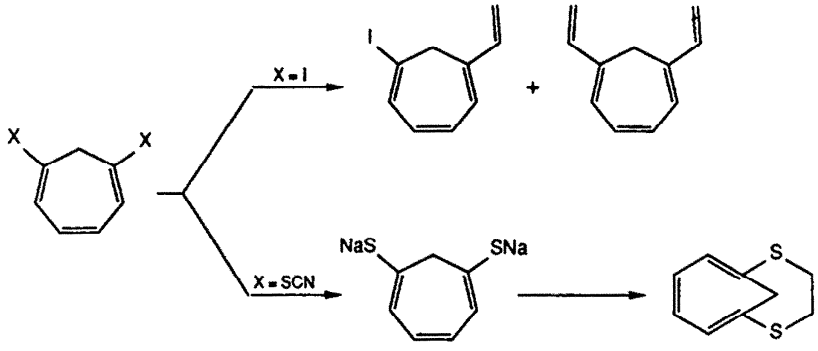


derivatives, further demonstrating the potential of cycloproparenes in synthesis. *Syn*-1,6:8,13-bismethanol[14]annulene (**133**) was synthesized recently via 1,6-diiodocycloheptatriene,[55] as illustrated in Scheme XXI. The cyclopropannulene **64** has also been utilized in the synthesis of **133**.[76]

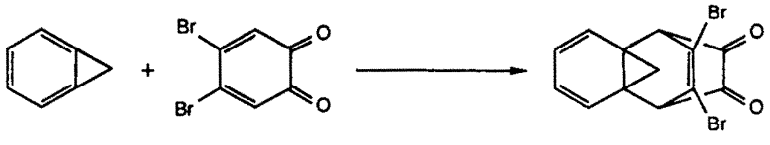
Benzocyclopropenes have a demonstrated potential as dienophiles, as evidenced by the formation of 1,6-methano[10]annulene from **1** and butadiene.[58] Other examples can be found in the reactions



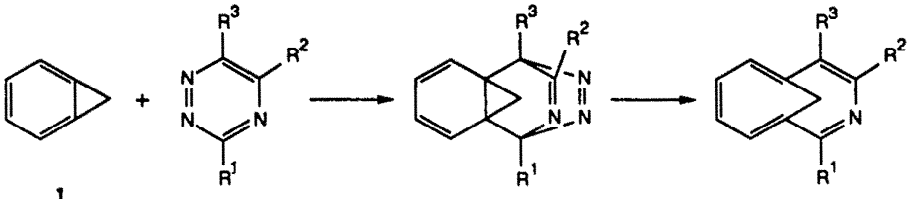
Scheme XXI[55].



of **1** with α-pyrone and 1,2,4,5-tetrazine-3,6-dicarboxylate.[4] The cycloadducts are thermally labile and undergo respective decarboxylation and deazetation. Benzocyclopropene and 4,5-dibromo-*o*-benzoquinone give **134**.[77] It has not been demonstrated whether the reaction proceeds via a concerted [π6s + π4s] pathway or an alternate nonconcerted process.



1 **134**



1

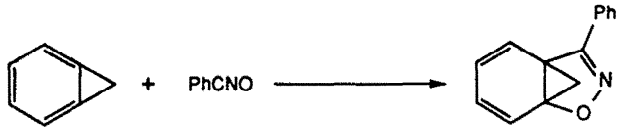
$R^1 = CO_2Et$, CN, H; $R^2 = R^3 = CO_2Et$

$R^1 = CO_2Et$; $R^2 = R^3 = H$

135

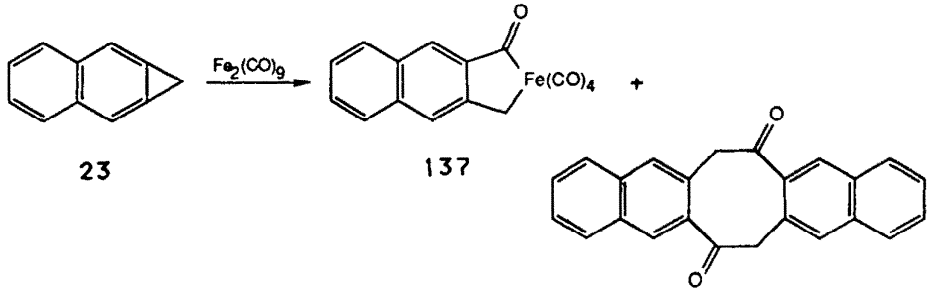
Benzocyclopropene has been used as a dienophile with substituted triazines[78] to give methanoaza[10]annulene derivatives such as **135**. When the R group is H, ultra-high-pressure techniques are required. The reaction of **1** with the parent triazine ($R^1 = R^2 = R^3 = H$) has not been affected.

Further cycloadditions involving benzocyclopropenes and reactants such as *p*-toluenesulfonyl azide, *p*-nitrophenyl azide, diphenylnitrilimine, ethyldiazoacetate,[79] and phenyl azide[80] have been unsuccessful. Benzocyclopropene has been shown to react with aryl nitrile oxides in a dipolar cycloaddition to yield stable (up to 130°C) bridged norcaradienes such as **136**.[81]



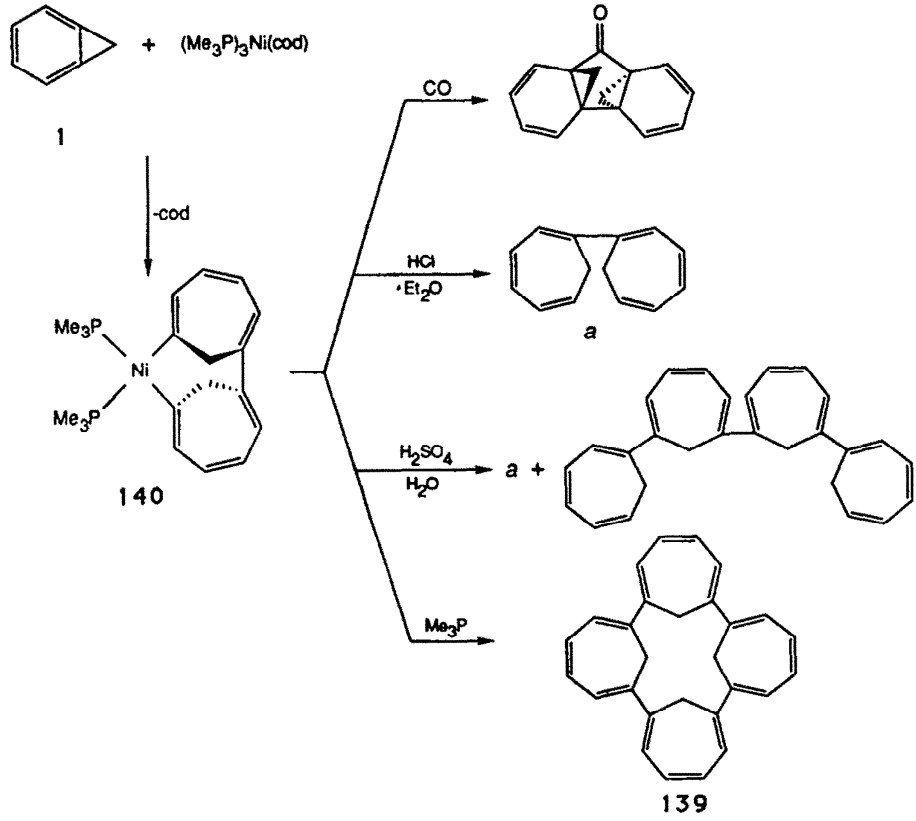
1 136

In anticipation that partial bond localization might lead to interesting π-complexes with metal carbonyls, benzocyclopropene and cyclopropa[b]naphthalene have been reacted with diiron nonacarbonyl.[82] With **1** only intractable materials were obtained; however, **23** yielded the stable metallacycle **137** and a trace of the dione **138**. No evidence of the desired π-complex was found. The co-condensation of benzocyclopropene with chromium atoms also failed to afford any volatile π-complexes;[83] upon exposure to air, only a C_7H_6 polymer was obtained.

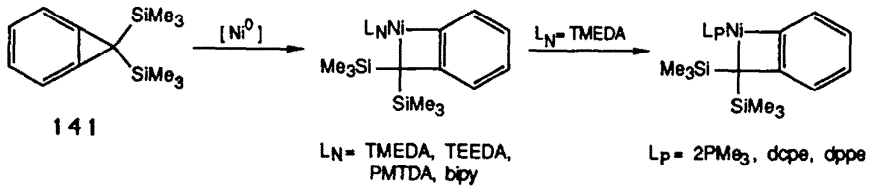


23 137 138

The observation that certain Ni(0) complexes catalyze the oligomerization of benzocyclopropene adds an important new dimension to the use of cycloproparenes in synthesis. For instance, conditions have been found for the cyclotetramerization of benzocyclopropene to yield the fascinating [24]annulene **139**.[84] A key intermediate is the bis-methano-bridged nickelacyclotridecahexaene **140** which, upon treatment with $P(CH_3)_3$, yields **139** by reductive elimination. Under different conditions, other products are observed (Scheme XXII). Other nickel(0) complexes

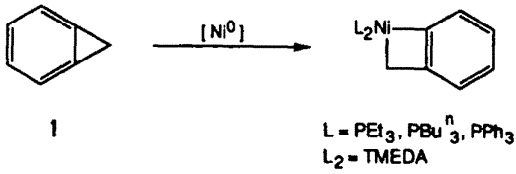


Scheme XXII[84].

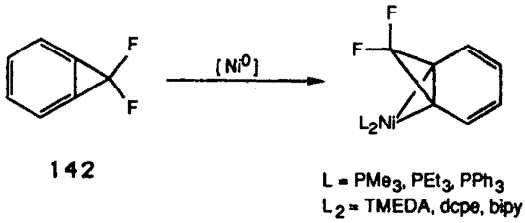


Scheme XXIII[86].

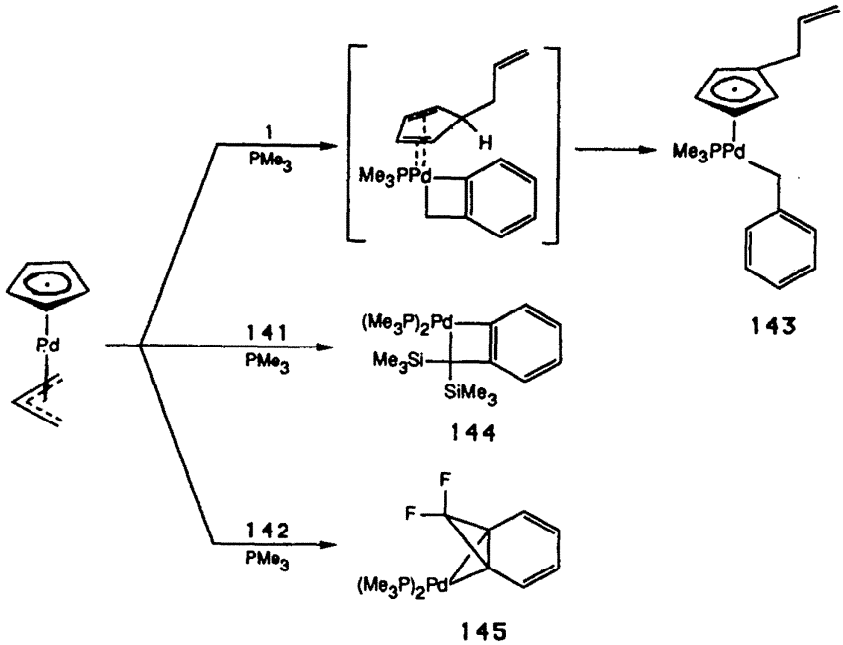
have been found to yield nickelacyclobutabenzene compounds by oxidative addition.[85] The bis(tri-



methylsilyl) derivative **141** reacts similarly to form a nickelacyclobutabenzene;[86] with L_N = TMEDA the nickelacyclobutabenzene undergoes ligand exchange smoothly with phosphorus ligands (Scheme XXIII). The difluoro derivative **142** reacts with several nickel(0) complexes to yield the propellane structure.[87]



Reaction of (η^3-allyl)(η^5-cyclopentadienyl)palladium with benzocyclopropenes **1**, **141**, and **142** and $P(CH_3)_3$ afforded the palladium complexes **143–145**, illustrated in Scheme XXIV.[88] Benzocyclopropenes **141** and **142** afford complexes that are analogous to reactions with nickel(0), whereas



Scheme XXIV[88].

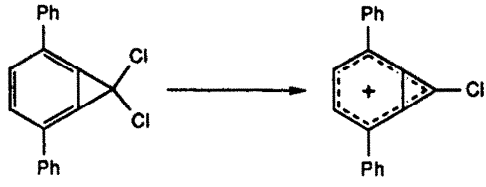
benzocyclopropene **1** gives a benzyl complex in which a metallacycle is presumably involved as an intermediate.

Birch reduction of benzocyclopropene is reported to give ring-cleaved products;[46] 1-methylcyclohexa-1,4-diene, toluene, and 1,2-diphenylethane are obtained in the ratio of 62 : 28 : 10.

5. THE BENZOCYCLOPROPENYL CATION AND ANION

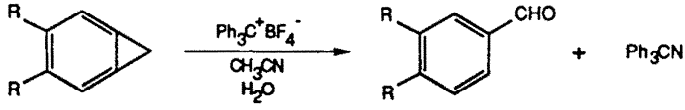
Although the benzocyclopropenyl cation **146** received theoretical attention as early as 1962,[89] the only experimental evidence available for years was the mass spectral fragmentation pattern of substituted cycloproparene derivatives.[4,8] Compound **94**, for example, shows a M_p-35 peak reasonably postulated as the benzocyclopropenyl ion **147**. Self Consistent Charge-Extended Hückel Molecular Orbital calculations reported in 1973[90] predicted stabilization of the parent ion by charge delocalization, and it was suggested that the parent ion might be isolable.

146



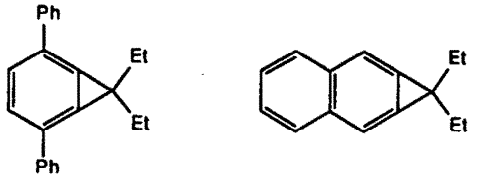
94 **147**

Indeed the parent ion and several derivatives have subsequently been generated in solution. Treatment of both **1** and **23** with tritylfluoroborate[91] yields the corresponding aryl aldehyde after hydrolysis; formation of the respective cation is implicated in this process.

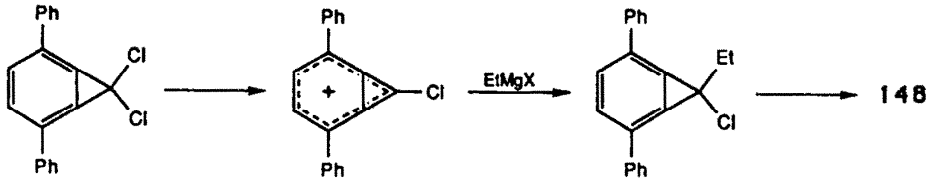


1 R = H
23 RR = benzo

In other cases the integrity of the benzocyclopropene skeleton is maintained. The *gem*-dichloride **94** and the naphthalene analog **13** can be alkylated with either Grignard or organolithium reagents.[14,64] Compounds **148** and **149** have been isolated from these reactions as illustrated in the case of **148**.

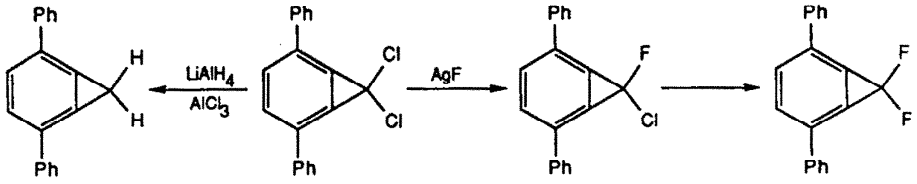


148 **149**



94 **147**

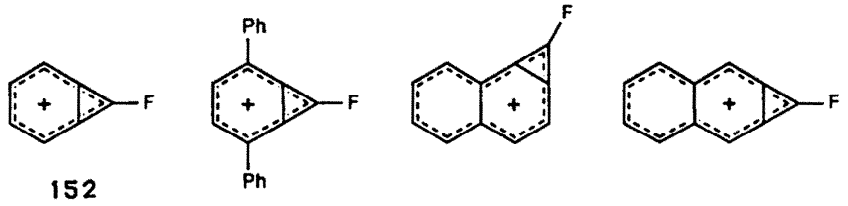
The reaction of **94** with silver fluoride or $LiAlH_4/AlCl_3$ provides further evidence for the benzocyclopropenyl cation. With AgF, **94** is converted to the *gem*-difluoro derivative **150**.[92] The reaction can also be terminated at the half-exchange product **151**.[93] $LiAlH_4/AlCl_3$ yields the corresponding hydrocarbon.[94] Reductions using only $LiAlH_4$ cannot be terminated at the exchanged product, and give only ring opening to the cycloheptatrienyl or benzyl derivatives.[64]



94 **151** **150**

There is a large body of spectroscopic evidence for the benzocyclopropenyl cations. The ^1H and ^{13}C NMR spectra of **147** have been recorded,[95] using solutions prepared by the dissolution of **94** in fluorosulfonic acid. The ion exhibits a resonance of 9.22 ppm for H_3 and H_4, which is deshielded *ca* 1.5 ppm from compound **94**. C_1 appears 71 ppm downfield (131.2 ppm) from its sp^3 counterpart in **94**. The cation has also been prepared by reaction of **94** with antimony pentachloride. A solution of this salt in chlorosulfonic acid gave spectra identical to those reported for the dissolution of **94** in fluorosulfonic acid.

Similar techniques have been used to generate 1-fluorocycloproparyl cations from 1,1-difluoro-1H-cyclopropabenzenes, -[a]naphthalenes, and -[b]naphthalenes.[15,32,96] The spectral data of selected compounds have been summarized in Table I. NMR assignments have been aided by the use of specifically labelled 2,5- and 3,4-dideuterio derivatives in the case of **152**.[97] Attempts to prepare the

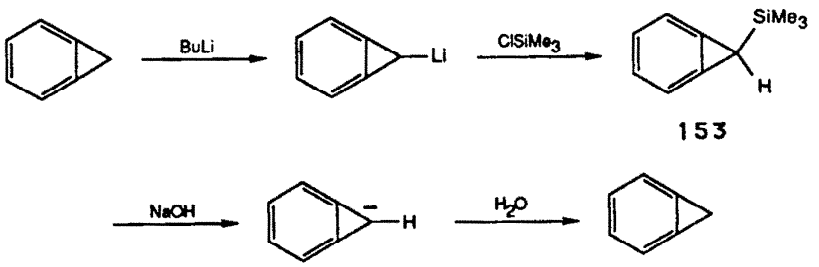


152

cycloprop[b]anthryl cation in an analogous manner have failed, however, probably due to the tendency of protonated dihalogenocycloprop[b]anthracenes to undergo polymerization rather than ionization to cations.[17] The cyclopropa[l]phenanthryl cation has been postulated as a reaction intermediate in the decomposition of **65** with *t*-butyl peroxide.[37]

The charge distribution in these ions has been estimated from the changes in the ^{13}C chemical shifts upon ionization.[95] Ion **147** and its fluoro analog show little delocalization of the charge into the two phenyl substituents. Approximately 45% of the charge resides in the three-membered ring.

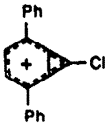
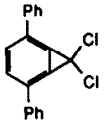
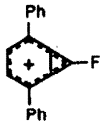
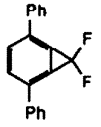
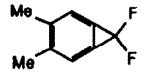
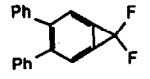
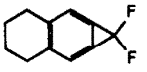
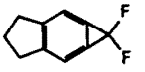
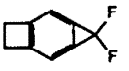
The low-temperature lithiation and conversion of benzocyclopropene to the trimethylsilyl derivative **153**, and cleavage of this compound with sodium hydroxide[98] provides compelling evidence for the existence of the anion **154**. The cleavage of **153** occurs 64 times more rapidly than benzyltrimethylsilane, indicating a pK_a of $\sim$36 for **1**. The use of these anions in synthesis has been described earlier.



153

154

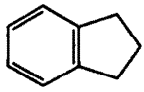
Table I. NMR Parameters of Benzocyclopropenyl Cations[a,b]

Compound	H2(5)	H3(4)	C1a(5a)	C2(5)	C3(4)	C1	Ref.
		9.22(s)	150.4	146.4	147.5	131.2	95
		7.70(s)	131.6	130.4	129.1	60.1	38,95
		9.38(s)	134.7	130.8	148.7	147.2	95
		7.58(s)	126.1	128.6	132.0	101.6	95
	8.40(m)	9.20(m)	141.1	119.8	153.8	148.1	95,96
	7.45(m)	7.45(m)	129.5	116.0	134.7	100.3	95,96
	8.20(d)		138.0	116.2	175.1	143.8	15
	7.31(t)		128.2	115.9	145.4	101.2	15
	8.35(d)		138.1	118.0	173.3	143.8	15
	7.57(t)		128.8	117.6	149.0	101.2	15
	7.95(d)		136.8	115.7	175.9	142.8	15
	7.24(tm)		127.4	115.4	146.3	101.0	15
	8.20(d)		138.9	112.3	183.0	145.9	15
	7.33(tm)		128.3	111.7	153.0	103.9	15
	8.04(d)		138.8	110.7	183.2	145.1	15
	7.14(t)		127.0	109.6	154.2	101.6	15

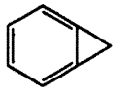
[a] Spectra reported in δ units.
[b] The corresponding cycloproparene is shown for comparison.

6. BOND LOCALIZATION AND STRAIN ENERGY

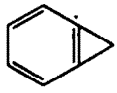
The concept of bond fixation advanced by Mills and Nixon[70] in 1930 has been an area of active investigation. The original experimental data on which the premise was based has been shown to be ambiguous,[99] and has been subjected to reinterpretation. A theoretical study[100] of the bond lengths and angles in indan and tetralin led to the conclusion that bond localization in indan should occur as depicted, and that the effect should be more pronounced in the more highly strained benzocyclobutenes and benzocyclopropenes.



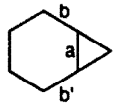
X-ray crystallographic data and thus exact bond lengths and angles are available for some cyclopropanes. These data are presented in Table II. The data indicate that some bond localization does occur, but it is remarkable that bond fixation is not in accordance with either Kekulé structure **1a** or **1b**; instead, three adjacent short bonds are found (b-a-b'). The bridging bond (a) is shorter



1a

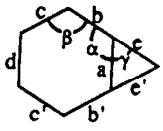


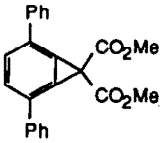
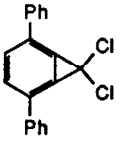
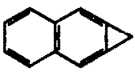
1b



than benzene (1.395 Å) and intermediate between cyclopropene (1.296 Å) and cyclopropane (1.510 Å).[101] The effect is most pronounced in the *gem*-disubstituted compounds and is less extreme in cyclopropa[b]naphthalene. The reader is referred to the theoretical study of Apeloig and Arad on this topic.[102]

Table II. Crystallographic Data of Benzocyclopropenes[a]



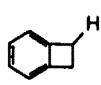
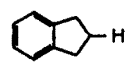
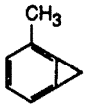
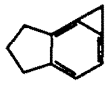
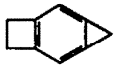
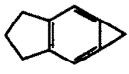
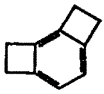
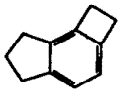
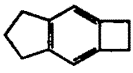
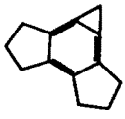
Compound	a	b(b')	c(c')	d	e(e')	α(α')	β(β')	γ(γ)	Ref.
	1.333	1.385 (1.389)	1.417 (1.421)	1.392	1.519 (1.520)	126.6 (126.3)	109.3 (109.6)	64.0 (64.0)	110
	1.35	1.39 (1.42)	1.40 (1.38)	1.39	1.47 (1.45)	128 (124)	108 (110)	62 (63)	111
	1.339	1.355	1.423	1.411	1.52	126.1	111.5		112
	1.368	1.337	1.437	1.439	1.504	124.9	114.7	62.9	103

[a] Bond lengths are in angstroms; bond angles are in degrees.

The strain energy of benzocyclopropene has been determined experimentally[103] from a silver-ion catalyzed methanolysis reaction, and is ~68 kcal/mol. This value is substantially higher than the total strain energy of cyclopropene (52.6 kcal/mol).[104] A similar methanolysis study for cyclopropa[b]naphthalene gave a value of 65–67 kcal/mol, and combustion calorimetry gave 67.8 kcal/mol.[103] Combustion data have also been obtained for dicyclopropa[b,g]naphthalene **60**,[105] yielding a strain energy of 166 kcal/mol. This represents a minimum value, since clean combustion of **60** was difficult to achieve. The strain energy of **60** is more than twice that of **23** and would seem to reflect the increased distortion induced by the second strained-ring fusion.

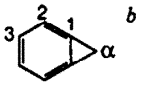
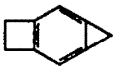
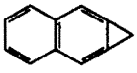
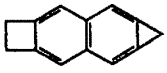
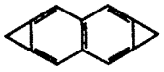
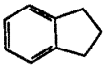
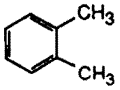
The ^{1}H NMR spectra of benzocyclopropenes exhibit fairly normal chemical shifts. The appearance of the protons in the usual aromatic region indicates little effect by structural distortion of the ring current. Data for several representative cycloproparenes are summarized in Table III. The protons of the methylene group appear as a characteristic singlet in the range 3.0 to 3.5 ppm.

Table III. ^{1}H NMR Data of Benzocycloalkenes[a]

Compound	Ar-H					Ref.
	7.19-7.15	3.11				112
	7.08-6.80	3.06	2.34 (methyl)			21
	7.04-6.82	3.18	3.24			33
	7.20-7.00	3.20		3.05-2.80	2.30-1.95	43
	6.85	3.08	3.08			33
	7.15	3.35		3.05-2.80	2.28-1.92	43
	6.88		3.14			113
	7.07-6.80		3.12	2.85-2.77	2.03	113
	6.91		3.08	2.86	2.00	113
		3.10	3.20			42
		3.16		3.00-2.70	2.35-2.05	42

[a] Spectra reported in δ units.

Table IV. ^{13}C NMR Data of Benzocycloalkenes[a]

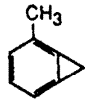
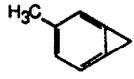
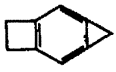
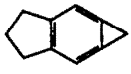
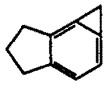
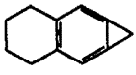
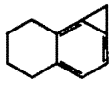
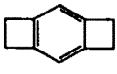
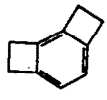
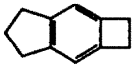
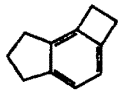
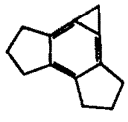
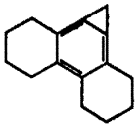
Compound	C-α	C1	C2	C3	C4	C5	C6	Ref.
	18.4	125.4	114.7	128.8	128.8	114.7	125.4	114
	19.9	119.6	135.9	148.0	121.0	112.4	126.0	69
	19.2	122.8	110.0	145.5	145.5	110.0	122.8	33
	18.6	123.4	112.3	136.7	136.7	112.3	123.4	114
	19.3	122.1	112.7	136.2	136.2	112.7	122.1	30
	19.9	122.8	113.5	140.1	140.1	113.5	122.8	34
	29.4	145.6	122.1	126.6	126.6	122.1	145.6	114
	33.8	144.0	124.4	126.2	126.2	124.4	144.0	114
	19.4	136.3	129.8	126.0	126.0	129.8	136.3	114

[a] Spectra reported in δ units.
[b] Numbering system is for convenience only.

The ^{13}C NMR spectra of the cycloproparenes are more greatly affected by ring strain. Typical chemical shifts are shown in Table IV. The effects of ring strain are clearly shown at C_2 and C_5, which show increased shielding from 130 ppm in *o*-xylene, through indan and benzocyclobutene, to 114.7 ppm in benzocyclopropene; however, the C_1 and C_6 carbons in the sequence xylene–indan–benzocyclobutene are deshielded (136 ppm–145.6 ppm), and C_1 and C_6 in benzocyclopropene are shielded (125.4 ppm). The shielding at the bridge carbons may be due to the special nature of the cyclopropyl group, which is noted[106] for substantial shielding. The other cycloproparenes exhibit similar patterns, with enhanced shielding at C_2 and C_5 with chemical shifts of 110–15 ppm, and shifts of 120–126 ppm for C_1 and C_6. The remaining aromatic carbons, C_3 and C_4, removed from the site of fusion, are essentially unaffected by ring strain. The narrow range (110–115 ppm) of shifts for C_2, even for the highly strained bis-annelated compounds, indicates that ^{13}C chemical shifts may not provide a reliable method to evaluate the strain of these compounds.

The UV spectral data of several benzocycloalkenes are recorded in Table V. The mono-annelated benzene derivatives show little influence of the small ring on the aromatic chromophore. Annelation of a second ring to a benzocyclopropene gives a more pronounced effect. The linearly fused bis-annelated systems exhibit a bathochromic shift with reduction in ring size. This shift to longer wavelength had been noted long ago[107] for dicyclobuta[a,d]benzene relative to durene, but is intensified in the benzocyclopropenes. The reverse trend is observed for the nonlinearly fused bis-

Table V. Electronic Spectra of Benzocycloalkenes[a]

Compound	λmax			Ref.	Compound	λmax			Ref.
 [b]	277	270	264	43		276	263	255	21
	271	265	259	113		284	277	270	21
	294	287.5	284	33		276.5	270	264	33
	292	283	274	43		280	272	266	43
	289	282	274	43		283	275	267	43
	286	280	276	113		275	269	266	113
	286	280	276	113		276	271	267	113
	275	268	247	42		279	270	-	42
	283	273	-	42					

[a] Wavelength maxima are in nanometers.
[b] Two other bands were recorded at 258 nm and 252 nm.

annelated systems; a bathochromic shift occurs with increasing alkyl ring size. This behavior has been rationalized[108] from the hyperconjugative abilities of the fused rings and changes in the configurational composition of the lowest excited singlet state.

The IR spectra of benzocyclopropenes exhibit a characteristic band at *ca* 1670 cm^{-1}, which has been attributed to the combination of a three-membered ring vibration and an aromatic 'double bond' stretching vibration. Examples are benzocyclopropene (1660 cm^{-1}) and cyclopropa[b]naphthalene (1673 cm^{-1}). Otherwise, the infrared spectra are simple, and reflect the symmetry of these molecules.

The rotational spectrum of **142**, measured in the X- and R-bands, has been analysed to give the rotational constants in the ground and first four vibrational states.[109] Analysis of the second-order Stark effect yields the dipole moment in the ground state (3.57 D) and first excited state (3.54 D)

for **142**. This high value implies considerable polarization of the π-electron framework; the most obvious rationalization of this value lies in a contribution from the benzocyclopropenyl cation.

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[3] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.* **78**, 500 (1956); *Ibid.* **80**, 2255 (1958).
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[6] Earlier reports describing the synthesis of benzocyclopropenes have been shown to be incorrect. See: S. C. De and D. N. Dutt, *J. Indian Chem. Soc.* **7**, 537 (1930); B. Halton, S. A. R. Harrison and C. W. Spangler, *Aust. J. Chem.* **28**, 681 (1975); A. Mustafa and M. Kamel, *J. Am. Chem. Soc.* **75**, 2939 (1953); G. W. Jones, D. R. Kerur, T. Yamazaki, H. Shechter, A. D. Woolhouse and B. Halton, *J. Org. Chem.* **39**, 492 (1974); A. G. Pinkus and J. Tsuji, *Ibid.* **39**, 497 (1974).
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