Developments in Cycloproparene Chemistry

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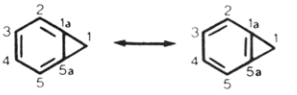
Brian Halton was born in Lancashire, England, and graduated with a B.Sc. (Honors) and Ph.D. from the University of Southampton and, more recently, with a D.Sc. from Victoria University of Wellington. After postdoctoral and teaching experience at the University of Florida, he moved to Victoria University in 1968 and has held the position of Reader in Chemistry since 1977. He was a British Council Scholar at the University of Reading in 1974–1975, a Fulbright Scholar and Visiting Professor at the University of Utah in 1981–1982, and President of the New Zealand Institute of Chemistry in 1986–1987. His current research interests are strained organic molecules, reactive intermediates and reaction mechanism, and organic photochemistry.

I. Introduction

Chemists continue to be fascinated by the imposition of stress and strain upon organic molecules. The attendant modification to reactivity that these changes bring has been used to advantage in many cases, and in particular for the synthesis of numerous natural products. Thus strained ring systems are unusually reactive and often unstable. By comparison, molecules that satisfy the criteria for aromaticity are found to have enhanced stability. The cycloproparenes are molecules in which a single carbon atom is fused across adjacent centers of an aromatic system and they set these features in juxtaposition.

The existence of cyclopropabenzene (**1**) as the most highly strained, isolable member of the ortho-fused series of aromatic compounds has been firmly established for almost a quarter of a century.[1] The molecule is surprisingly stable and has a strain energy of 68 kcal/mol associated with the fused ring system.[2] As a result of improved synthetic methods, other aromatic systems containing 1,2-methylene fusion and cyclopropabenzenes further strained by fusion to a second carbocyclic ring system have become available. The fascination of this series of hydrocarbons and their derivatives lies in the desire to establish the limits to which stress and strain may be imposed upon the benzenoid framework and to delineate the consequential influences upon bonding, structure, and chemical reactivity. Although numerous studies have addressed these questions, many facets still remain to be defined.

The obvious interest of the experimentalist in strained organic molecules has been matched almost by that of the theoretician in his search for suitable models for developing the concepts of chemical bonding and aromaticity. The cycloproparenes fulfil these needs because of the expectation[3] of partial aromatic bond localization, **1a** vs **1b**, and consequent bond length al-



1a **1b**

ternation in the aromatic ring. The species **2** and **3**, derived from **1** by C(1)–H bond heterolysis, and **4** by bond homolysis, as well as the derived ketone **5** and the methylene derivative **6**, are also of interest in these respects.

The cycloproparenes have been the subject of two earlier reviews[4] and a research account and report;[5] a detailed review[6] of cyclopropene chemistry has only incidental coverage of the cycloproparenes. The present contribution aims to provide comprehensive, yet critical, coverage of the literature from the time of the last re-

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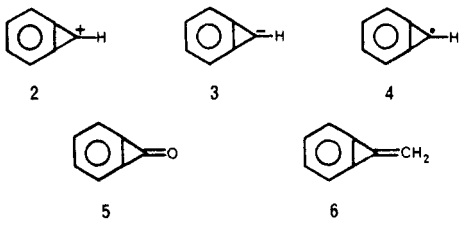
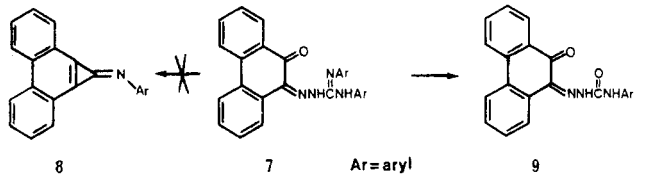


view and to indicate the likely direction of future research. It should be noted, however, that for the purposes of continuity the important earlier findings are included herein. *Chemical Abstracts* has been reviewed through Vol. 109, 1988. For convenience the term "cycloproparene" will be used throughout this review despite the fact that fusion nomenclature, viz., use of the prefix *cyclopropa*, can only be applied when "at least two rings of five or more members" are present (IUPAC Rule A 21.3). Thus while 1*H*-cyclopropa[*b*]-naphthalene is correct for **36**, 1*H*-cyclopropabenzene is incorrect for **1**. Chemical Abstracts Service and IUPAC are unanimous in the nomenclature of **1** as bicyclo-[4.1.0]hepta-1,3,5-triene (**1a**). As will be appreciated, any strict adherence to this rule provides nomenclature for the parent member that not only differs from that of its higher homologues but also could be taken to imply a bond-localized structure. In addition, compounds **5**, **6**, and **172a–c** are named systematically as 7-oxo-, 7-methylene-, 7-aza-, 7-thia-, and 7-selenabicyclo[4.1.0]hepta-1,3,5-triene, respectively.

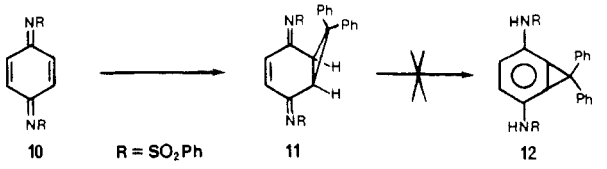
II. Synthesis of the Cycloproparenes

A. Historical Approaches

The earliest claim to the synthesis of a cycloproparene appeared in 1930. The decomposition of a series of arylimino semicarbazones **7** derived from 9,10-

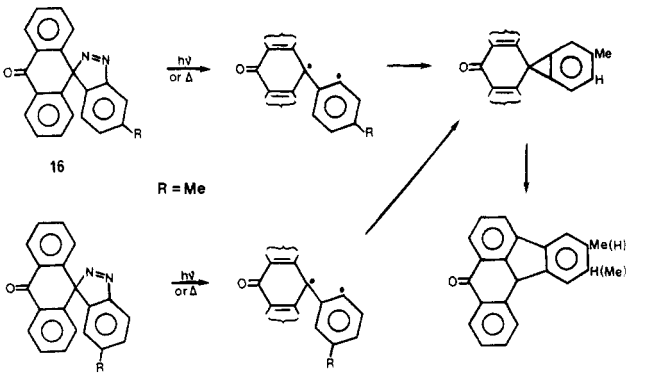


phenanthraquinone was proposed[7] to result in the iminocyclopropa[*l*]phenanthrenes **8**. However, a reinvestigation[8] of these reactions has provided only the 4-aryl semicarbazones **9**. While the addition of secondary diazoalkanes to quinone imides, e.g., **10**, gives

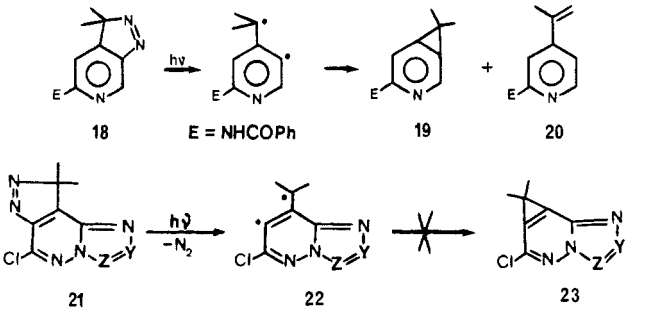


products whose properties match those reported[9] by Mustafa and Kamel in 1953, the products[10] are not cycloproparenes, e.g., **12**, but the unrearranged bicycloheptenes, e.g., **11**. The aromatization of **11** and analogues has yet to be accomplished.[10] Thus the earliest authenticated[11] claim to the synthesis of a cycloproparene appeared 25 years ago, some 75 years after W. H. Perkin Jr. noted[12] that cyclopropabenzene was yet to be prepared!

SCHEME I

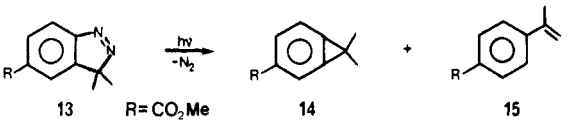


SCHEME II

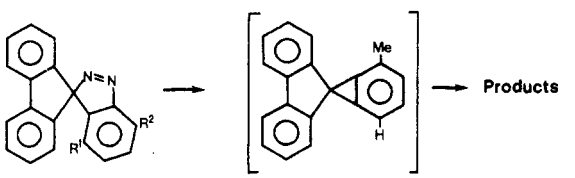


B. Photolysis of 3*H*-Indazoles and Spiro-3*H*-pyrazoles

In 1964 Anet and Anet[11] found that photolysis of the 3*H*-indazole **13** led to nitrogen loss and the formation of the cyclopropabenzene **14** in addition to the styrene

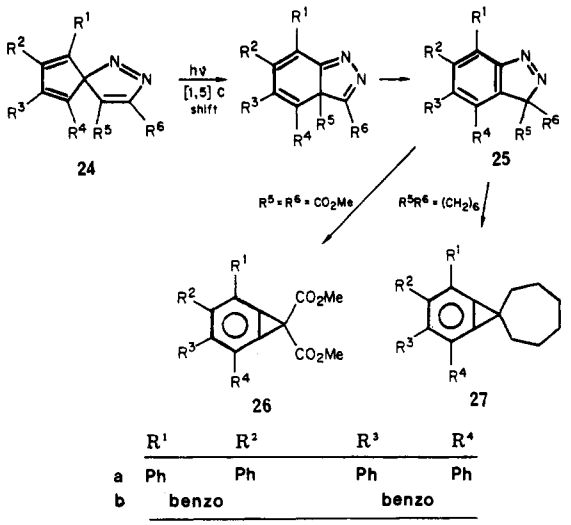


derivative **15**. This method, the first for the synthesis of a cycloproparene, received a degree of attention initially,[4,5] but difficulties associated with preparation of the substrates and the limitation to geminally disubstituted derivatives (3-monosubstituted indazoles exist in the alternative 1*H*-tautomeric form) have negated its value as a viable synthetic route. More recently, the photolysis and thermolysis of a number of anthrone-10-spiroindazoles, e.g., **16**, have been examined[13] and the intervention of spirocyclopropareness in the formation of products has been established (Scheme I). Such intervention had been suggested previously[14] in the thermolysis and photolysis of spirofluorene analogues, and this has now been confirmed[15] for the methyl-substituted substrates **17a,b**.



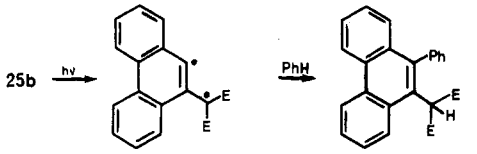
The most significant application of the 3*H*-indazole route lies in the recent synthesis of the first cyclopropapyridine derivative. Streith and co-workers[16] have found that photoexcitation of the –N=N– moiety of **18** leads to the cyclopropa[*c*]pyridine **19** (24%) (Scheme

SCHEME III



II) in competition with the styrylpyridine **20** (26%); unchanged starting material was recovered in 16% yield. Compound **19** is a crystalline solid (mp 114–116 °C) stable when stored in an inert atmosphere. An analogous and comprehensive study[17] of the polyaza tricycles **21** has shown that products derived from diradical **22** do not include the corresponding cyclopropaheteroarene **23** or compounds derived from its intervention. In these cases the pincing effect of the fused five-membered ring pushes the radical centers of **22** too far apart for bonding to be a viable reaction pathway.

The spiro-3*H*-pyrazole route to cycloproparenes, e.g., **26a** and **27a**, developed by Dürr and his group[18] (Scheme III) have received scant attention in the past decade. Nonetheless, it is noteworthy that spirocycle **24b** ($R^5 = R^6 = CO_2Me$) provides indazole **25b** ($R^5 = R^6 = CO_2Me$) as a minor but isolable product of thermolysis (Scheme III).[19] Photolysis of this latter compound in benzene does *not* provide[19] cyclopropa[*l*]phenanthrene **26b** but affords the 9,10-disubstituted phenanthrene **29**. In view of the high strain of cyclopropa[*l*]phenanthrene (see section II.C.3b) it seems likely that diradical **28** inserts into the solvent in preference to ring closure.



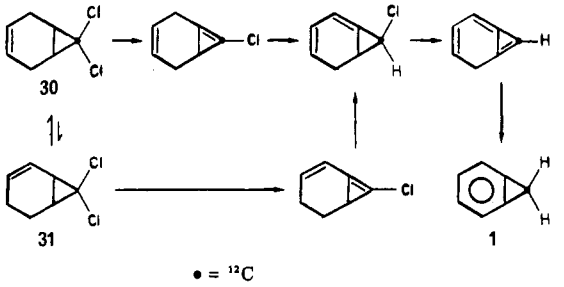
C. Bicyclo[4.1.0]heptenes as Precursors

The method of choice for cycloproparene synthesis involves the construction and subsequent aromatization of the bicyclo[4.1.0]heptane ring system.[4,5] The methodologies that have been developed fall into three categories, each of which depends upon the removal of suitably located substituents from the bicyclic framework.

1. *From 7,7-Dihalobicyclo[4.1.0]heptenes*

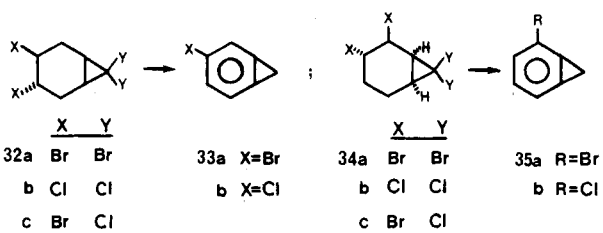
The use of 7,7-dihalobicyclo[4.1.0]heptenes provides a method of synthesis of cycloproparenes unsubstituted at the 1-position. The method, developed by Billups and co-workers,[20] has been applied successfully to provide a variety of different ring systems that incorporate the cyclopropabenzene moiety.

SCHEME IV

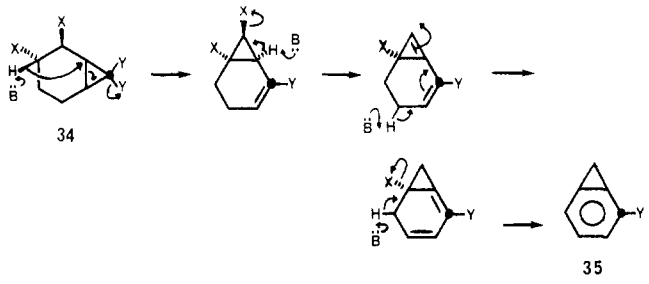


The Billups procedure involves double dehydrohalogenation and aromatization and proceeds via high-energy ring-fused intermediates as illustrated in Scheme IV for the formation of **1**. The pathway depicted is supported by an elegant labeling study. Thus Prestien and Günther[21] have shown that addition of dichlorocarbene-^{12}C (from $^{12}CHCl_3$) to cyclohexa-1,4-diene provides **30** specifically labeled at the 7-position. The cyclopropabenzene (**1**) produced upon dehydrochlorination of **30** is labeled exclusively at Cl as evidenced by the absence of the resonance due to this carbon atom (18.4 ppm) in the ^{13}C NMR spectrum. This shows that the route from **30** to **1** cannot involve skeletal rearrangement. Insofar as the synthesis of **1** itself is concerned, the site of unsaturation in **30** is not critical since the isomeric Δ^2-olefin **31** affords **1** in essentially the same yield under the same conditions even though the reaction is somewhat slower.[22,23] However, it should be noted carefully that the original[20] experimental procedures for the synthesis of **1** have now been markedly improved upon. Okazaki and his group[24] have increased the yield of **30** from cyclohexa-1,4-diene by ca. 14%; sodium hydroxide and the phase-transfer catalyst benzyldimethyl(2-hydroxyethyl)ammonium chloride are used in place of potassium *tert*-butoxide in the generation of dichlorocarbene. Furthermore, a simpler procedure for the extraction of **1** from the reaction mixture improves the quantity isolated by ca. 24%. The combined effect is that the yield of **1** from cyclohexa-1,4-diene is approximately doubled (from 12–16% to 28–35%) while the scale of operation can be increased simultaneously by a factor of 6 to give almost 0.5 mol of **1**; the highly odoriferous cyclopropabenzene is thus a readily available compound!

The presence of unsaturation in the bicycloheptene precursor is not a prerequisite for cyclopropabenzene formation provided that an appropriate number of leaving groups are present. Thus 2-bromo-7,7-dichlorobicyclo[4.1.0]heptane loses 3 mol of hydrogen halide upon treatment with *t*-BuOK and gives **1** in 33% yield.[25] In all probability the reaction proceeds via olefin **31**. Similarly, tetrahalides **32** afford[26] 3-halo-

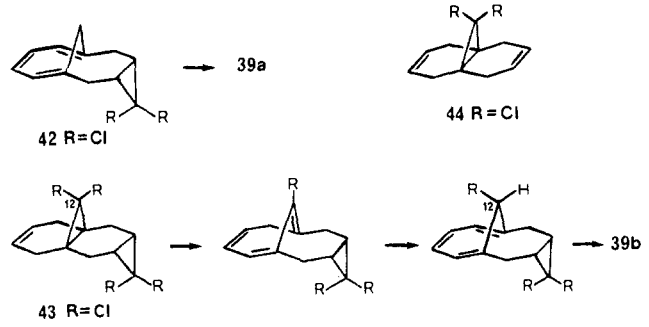


SCHEME V



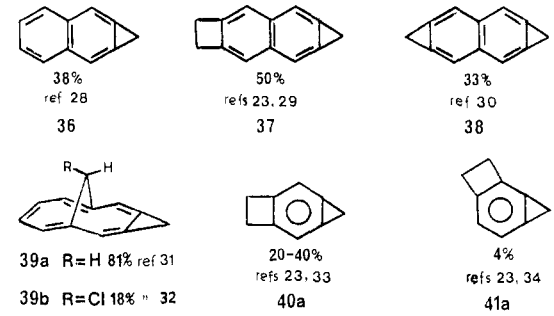
cyclopropabenzenes **33** in ca. 50% yield. The fact that **32b** partially labeled at C7 with ^{13}C gives **33b** with the label at Cl only and that the "mixed" halide **32c** gives 3-bromocyclopropabenzene (**33a**) exclusively shows that the triselimination proceeds without measurable skeletal rearrangement,[27] presumably by a pathway analogous to that of Scheme IV. A different situation pertains with the 2,3,7,7-tetrahalides **34a–c**. While **34a** and **34b** provide the corresponding 2-halocyclopropabenzene **35a** (48%) and **35b** (28%), respectively, **34c** gives a mixture of **35a** and **35b** in which the skeletally rearranged isomer is the *major* product.[27] When **34c** is partially labeled with ^{13}C at C7, the elimination sequence yields bromide **35a** without skeletal rearrangement whereas the C2–Cl moiety of **35b** arises by migration of the C7-labeled center and one of its attendant chloro substituents. The path by which **35** is obtained with retention of the label at C7 is presumed to involve the Billups–Günther mechanism of Scheme IV. On the other hand, the mechanism for the rearrangement is uncertain but it could proceed as indicated in Scheme V.

The success of the Billups synthesis is illustrated by Chart I, which depicts the range of fascinating compounds currently available.[28–34] Compounds **36–40** demonstrate that with skillful application the method is viable for linearly annelated analogues that can be strained further by fusion to a second small ring. Except for **39** and **41a** (see below) each of these compounds results from a precursor in which the 7,7-dichlorobicyclo[4.1.0]hept-3-enyl moiety is in place. The [10]annulene derivatives **39a** and **39b** are formed from **42** and **43**, respectively. While **42** may be regarded as

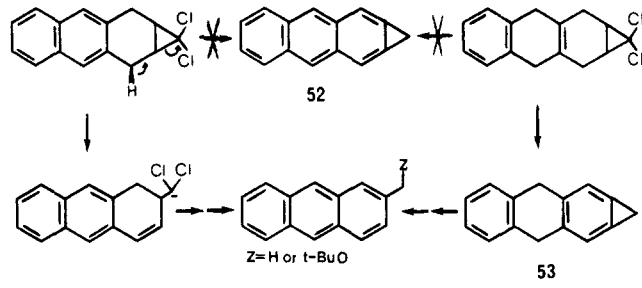


an analogue of **30** which delivers **39a** by the accepted mechanism,[31] the conversion **43** → **39b** deserves comment. Treatment of **43** with *tert*-butoxide affords **39b** directly but in low yield.[32] The formation of 1,6-methano[10]annulene from **44** under essentially the same reaction conditions has been described,[35] and an analogous path involving a bridgehead olefin is likely to operate; base-catalyzed epimerization at C12 is presumed to lead to **39b** as the thermodynamically more stable isomer.

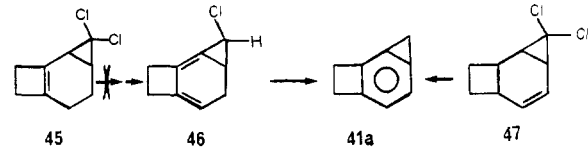
CHART I

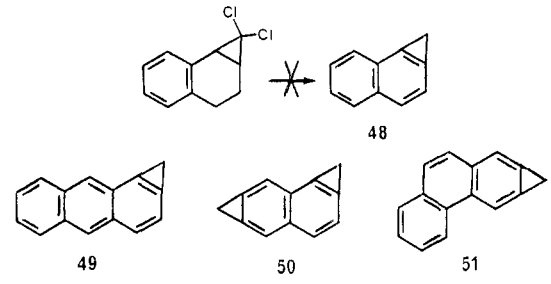


SCHEME VI



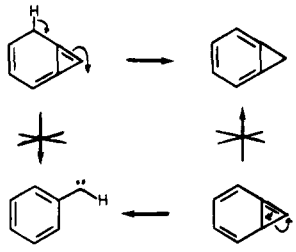
Whereas the synthesis of "rocketene" **40a** is uneventful,[23,33] an extension of the study to the angular isomer **41a** has not been straightforward. In an elegant study[23,34] Garratt and his colleagues found that tricycle **45** failed to aromatize under the normal dehydrohalogenation conditions and, while **41a** can be obtained from **47**, the yield is a meager 4–10%. Similar difficulties have been experienced[22–24] with attempted syntheses of **48–50**. These serve to illustrate that the





Billups procedure is unlikely to succeed when the endothermic migration of a tetrasubstituted olefinic linkage is required (cf. **45** → **46**) and/or when loss of HX can occur in two distinct ways. Furthermore, attempts to obtain 1*H*-cyclopropa[*b*]phenanthrene (**51**)[36] and 1*H*-cyclopropa[*b*]anthracene (**52**)[23,29] (Scheme VI) have also failed. In these cases antiperiplanar opening of the three-membered ring is likely to be triggered by abstraction of the pseudoaxial benzylic proton and formation of a cyclopropylcarbinyl anion. At the time these studies were performed, it was thought that **52** could have low stability because of bond fixation. However, the synthesis of this,[37,38] **51**,[36] and **53**[37] have recently been effected from 1,6-dihalobicycloheptenes

SCHEME VII

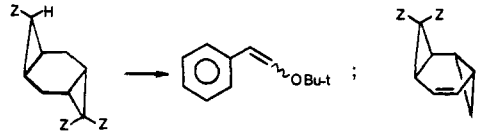


(see section II.C.2) and the compounds have moderate thermal stability. From these various studies it must be concluded that the bisdehydrohalogenation of 7,7-dihalobicyclo[4.1.0]heptene derivatives is restricted to the synthesis of linear analogues in the benzene and naphthalene series.

The existence of the highly strained rocketenes **40a** and **41a** as isolable compounds with moderate thermal stability[23] and of the dicyclopropparene **38** as a shock-sensitive crystalline solid that decomposes explosively upon melting[30] has extended the limits to which stress and strain may be imposed upon the benzenoid framework. Moreover, the isolation of these compounds raises the question of existence of the dicyclopropparenes **54** and **55**. It has been suggested[30] that **55** may rep-

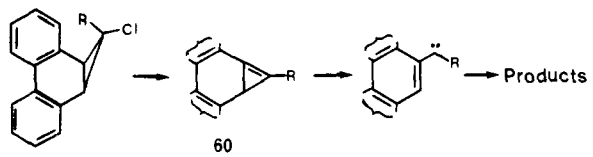
54 55 56

resent the limit for characterization at ambient temperature, whereas **56** is likely to be beyond the limits of detection.[39] Trisdehydrohalogenation of the *anti*-tricyclooctane **57** gives an *E*/*Z* mixture of the styrene shown by a path that avoids cyclopropparenes,[40] and attempted aromatization of tricyclooctene **58** is without success.[41]



57 Z = Cl 58

Modification of the Billups method to "locked" norcaradiene substrates is also without success. Thus treatment of **59** with *t*-BuOK does not yield the cor-

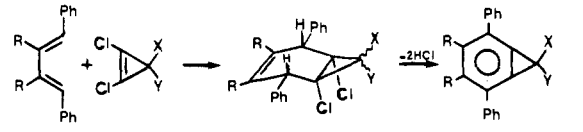


59 R=H or Cl 60

responding cyclopropa[*l*]phenanthrene.[42] There is no doubt that bicycloheptatriene **60** is formed but it provides products of either nucleophilic addition to the strained olefin or via ring cleavage to phenanthrylcarbene, depending upon the reaction conditions.[42] The propensity for bicyclo[4.1.0]hepta-2,4,6-trienes to undergo ring cleavage to aryl carbenes (or cycloheptatetraenes) under thermal conditions is well documented.[43] However, in the context of cyclopropparene synthesis it is noteworthy that bicyclo[4.1.0]hepta-1,3,6-trienes aromatize whereas their 2,4,6-isomers do not (Scheme VII).

2. From 1,6-Dihalobicyclo[4.1.0]heptenes

The early development of cyclopropparene chemistry saw the double dehydrohalogenation of 1,6-dihalobicyclo[4.1.0]hept-3-enes, e.g., **61**, provide a high-



61

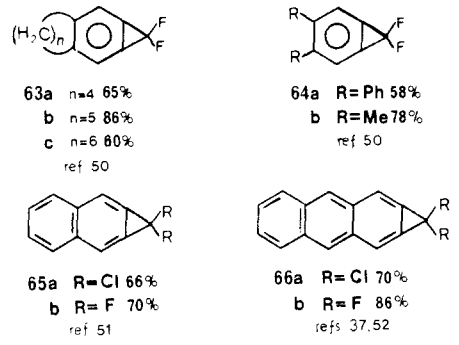
	R	X	Y
62a	H	Cl	Cl
b	H	F	F
c	H	Cl	F
d	–	Cl	Cl
	RR=benzo		

yielding route to compounds substituted at the 1-position. In particular, the use of 1,6,7,7-tetrahalogenated synthons provides *gem*-dihalocyclopropparenes, e.g., **62**, which subsequently may be converted into other derivatives.[4] The bicycloheptene substrates are easily prepared from cycloaddition of an appropriate diene to a perhalocyclopropene,[6,44] and they have been subjected to detailed scrutiny in recent times. Early studies mirrored the pioneering work of Law and Tobey[45] in assigning configuration to the bicycloheptenes, but it transpires that the expected [4 + 2] endo addition of the cyclopropene is not always followed. By the use of crystallographic and NMR methods Apeloig[46] and Müller[47] have shown that a cyclopropene with a bulky flagpole substituent at the sp^3 center (C3) adds in an exo sense to an (*E*)-1-substituted 1,3-butadiene; the cyclopropene C3 atom and the diene C1 substituent are located on opposite faces of the six-membered ring; cf. **61**. With 3-unsubstituted cyclopropenes endo addition predominates.[46] A consequence of these findings is that the presumed[48,49] syn eliminations to give cyclopropparenes **62** are in fact normal antiperiplanar eliminations from **61**.

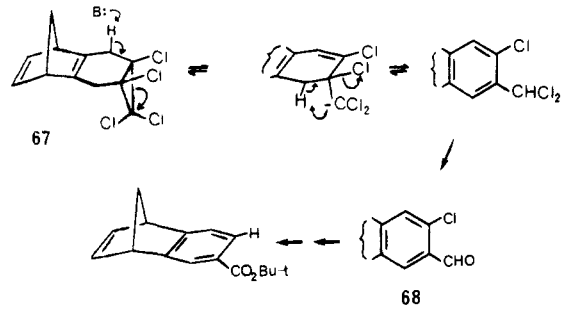
The methodology described has been elegantly extended by Müller and his co-workers in Geneva[50-52] to give the range of *gem*-dihalocyclopropparenes depicted in Chart II. Much of the success stems from effective syntheses of 2,3-bridged buta-1,3-dienes which have allowed for progression through the linear acene series and provided[52] the first cycloprop[*b*]anthracenes **66**; *gem*-difluoride **66b** is a stable crystalline solid (mp 190 °C dec). The early synthesis of *gem*-difluorocyclopropabenzene using this methodology has been markedly improved upon, and the compound is now easily available in 50-g quantities from 1,6-dichloro-7,7-difluorobicyclo[4.1.0]hept-3-ene.[53] In addition, the synthesis of **64b** (78%) reported by Müller[50] in 1986 has now been claimed by Neidlein[25] but the yield (54%) is noticeably lower.

In some cases aryl esters are isolated from 1,6,7,7-tetrahalobicycloheptenes instead of 1,1-dihalocyclopropparenes.[48,54] It is known that the isolable *gem*-dichloro- and *gem*-dibromocyclopropparenes, e.g., **62a**, react with alcohols to yield aryl esters,[4,48] and thus a route via the cyclopropparene is plausible. However, it has been suggested[55] that an alternative course of dehydrohalogenation, which involves antiperiplanar opening of the three-membered ring and bypasses a

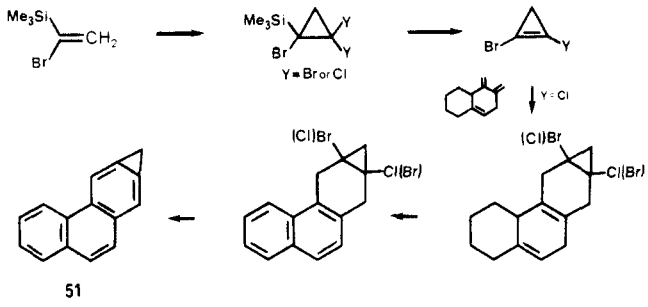
CHART II



SCHEME VIII



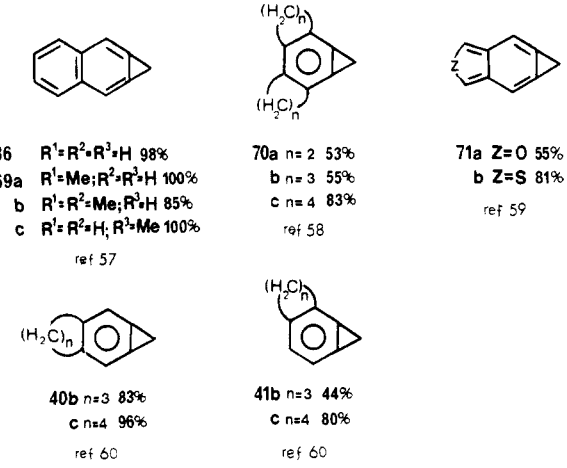
SCHEME IX



cyclopropparene, may operate in these cases. Thus **67** affords a non-chlorine-containing *tert*-butyl ester in 35% yield, for which the pathway depicted by Scheme VIII has been proposed. The final steps of the sequence require "nucleophilic attack at the aromatic chlorine and a different final hydrolysis step".[55] Some support is provided by the isolation of chloro aldehyde **68** (5%) from the reaction of **67** with *t*-BuOK in *tert*-butyl alcohol (Scheme VIII). The recent structure assignments of the tetrahalobicycloheptenes discussed above show[46,47] that the configuration of the bridging CCl_2 moiety in, e.g., **61**, is such that no antiperiplanar hydrogen atom is available, and consequently opening of the three-membered ring cannot operate by this mechanism. However, such cleavage in the attempted synthesis of **51** and **52** by the Billups procedure is entirely reasonable as is depicted in Scheme VI.

The most significantly advance in cyclopropparene synthesis in recent years stems from the ready availability of 3-unsubstituted 1,2-dihalocyclopropenes (Scheme IX).[36,56] These compounds have proved to be effective dienophiles in Diels–Alder cycloadditions with for example *o*-quinodimethanes, and they can be used in situ. Subsequent double dehydrohalogenation (Scheme IX) thus provides an alternative method for the synthesis of parent 1*H*-cyclopropparenes. The advantage of this procedure lies in the ease of dehydrohalogenation (which usually proceeds in good yield and

CHART III

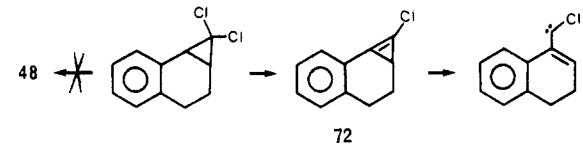


frequently at temperatures below −20 °C) and the fact that no π-bond migration is required. Thus the moderately stable cyclopropparenes **51–53**, which are unavailable from the Billups procedure, are obtained in yields of 89[36] and 42 and 75%,[37] respectively, by this method. Further applications have provided[57–60] the compounds shown in Chart III, and these bear testimony to the fact that many highly strained ring systems can be generated and characterized with comparative ease.

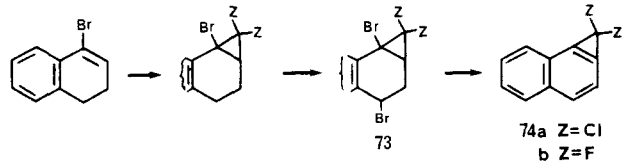
3. *From Other Bicyclo[4.1.0]heptenes*

The use of other bicycloheptenes variously substituted with leaving groups as potential cyclopropparene synthons has received increased attention. Compounds thus far examined have carried halide, carboxy, sulfur and selenium derivatives as well as removable hydrocarbon bridges as the substituents.

(*a*) *By Dehydrohalogenation.* Attempts to synthesize 1*H*-cyclopropa[*a*]naphthalene (**48**) from the angular 7,7-dichlorobenzobicycloheptane by application of the



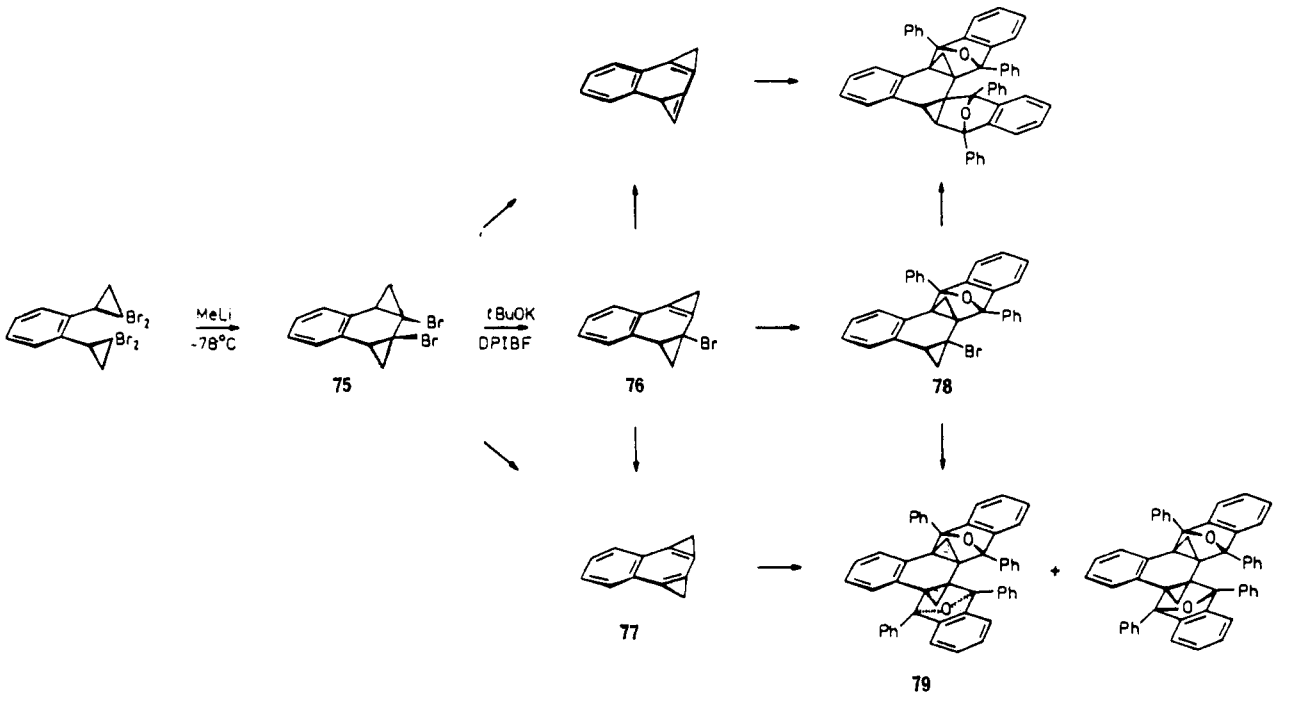
Billups procedure were without success as the intermediate chlorocyclopropene **72** opens to carbene.[5,22,34] In order to circumvent similar difficulties Müller and Thi devised[61] a more subtle approach to *gem*-dihalides **74** by blocking elimination from the benzylic cyclo-



propane center. Thus **73** serves as a progenitor to pure solutions of **74** from dehydrobromination at −78 °C. The compounds are stable to ca. −30 °C in solution but chloride **74a** is less stable than fluoride **74b**.

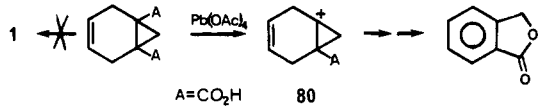
A further application of the dehydrohalogenation methodology has been aimed at the synthesis of dicyclopropanaphthalene **77**. Though unsuccessful the study[62] has uncovered the delightful chemistry depicted by Scheme X. Dehydrobromination of tricyclooctane

SCHEME X



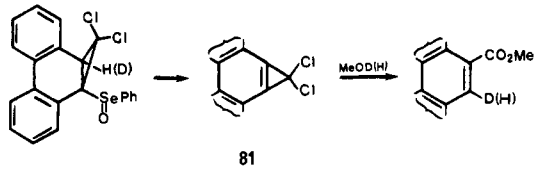
75 is rapid but none of 77 could be detected in the range −70 to +20 °C. In the presence of excess base and with diphenylisobenzofuran as trapping agent, three bisadducts are formed (Scheme X). When 1 mol equiv of base is employed, adduct 78 is isolated, and subsequent separate treatment of this compound to the same reaction conditions gives the *same* three bisadducts in the *same* ratio. Adduct 79 is the major product and is accounted for by elimination from 78, giving styrene, which is preferentially trapped by *anti* addition. Thus in the stepwise dehydrobromination of 75 the constrained cyclopropene 76 is trapped as 78 more rapidly than it forms dicyclopropareno 77 and it is unlikely that 77 is involved at all.

(*b*) *By Removal of Non-Halogen Bridge Substituents.* The lead tetraacetate bisdecarboxylation and aromatization of bridgehead dicarboxybicyclo[4.2.0]octenes has provided a viable path for the synthesis of cyclobutarenes,[63] but it does not lend itself to modification for cyclopropareno synthesis.[64] Rather than give the strained aromatic, e.g., 1, opening of the intermediate cation, e.g., 80, occurs and isobenzofuran-1(3*H*)-ones are



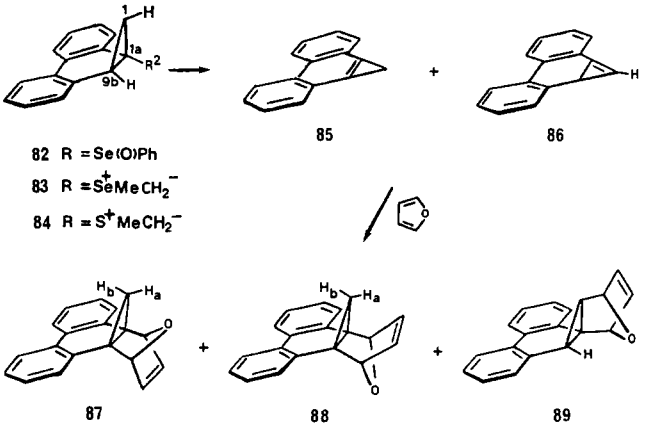
obtained. However, the removal of suitable bridge substituents has provided the highly reactive 1*H*-cyclopropa[*l*]phenanthrene ring system, which has proved to be inaccessible by other routes.[19,42]

The existence of the cyclopropa[*l*]phenanthrene ring system was established by the generation of 81 from syn



elimination of benzeneselenenic acid (PhSeOH) across the 1a,9b-positions of the dihydro progenitor.[65] Under the conditions necessary for selenoxide elimination, 81 is unstable and the product isolated is methyl phenanthrene-9-carboxylate. Complementary labeling studies are unambiguous in showing that a species with the symmetry of 81 is involved, and the subsequent ring opening of this *gem*-dichloride is fully compatible with the known chemistry of the cyclopropareno ring system.[4,5] An extension of this approach to selenoxide 82 results in 9-(hydroxymethyl)phenanthrene, and 1*H*-cyclopropa[*l*]phenanthrene 85 is most likely involved.[66]

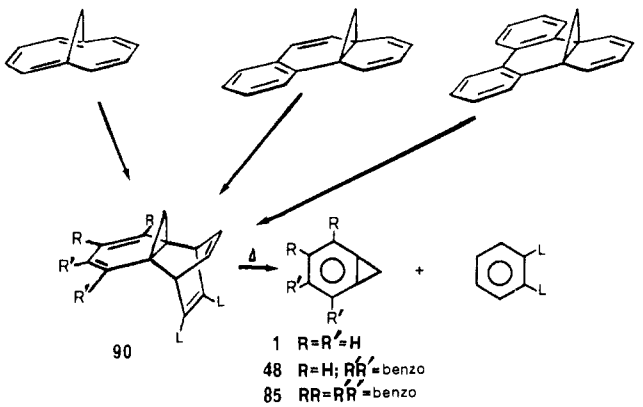
Definitive evidence for the formation of 85 comes from the syn elimination of dimethyl selenide from ylide 83. When the corresponding dimethylselenonium



tetrafluoroborate is allowed to react with *tert*-butoxide in the presence of furan, ylide 83 is formed, dimethyl selenide is ejected, and the adducts 87 (20%), 88 (13%), and 89 (7%) are isolated.[67,68] Moreover, Müller has subsequently discovered that the sulfur ylide 84 behaves in a similar manner.[66] The isolation of 87–89 requires the intervention of both 1*H*-cyclopropa[*l*]phenanthrene 85 and its 1a*H*-isomer 86. The fact that 87 and 88 form the major proportion of the product mixture is consistent with the predominant abstraction of the benzylic 9b-proton of 83 and preferential formation of the

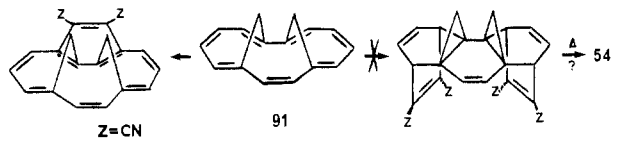
strained aromatic **85**. In the absence of trapping agent no discrete hydrocarbon products are isolated. This is not untoward in light of the stability of **85** (see below).

(*c*) *By Alder–Rickert Cleavage.* The route developed by Vogel and his group in 1965 to provide the original synthesis of cyclopropabenzene[1] has been elegantly extended by him in recent times. Thus, with painstaking care, appropriate hydrocarbons have been obtained for reaction with dienophile (usually dicyanoacetylene) to yield propellanes **90**, which may be viewed

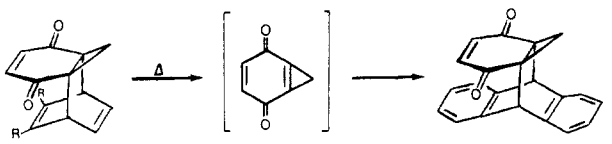


as hydrocarbon-bridged cycloproparenes. Alder–Rickert cleavage of **90** leads to **1** (45%; from the dimethyl acetylenedicarboxylate adduct),[1] **48** (83%),[69] and **85**.[67] Whereas **1** is a stable (but highly odoriferous) liquid, **48** decomposes upon melting at 20 °C and **85** is stable only for a few days at −78 °C!

The retrodiene route outlined above would seem to have potential for the synthesis of dicycloproparenes **54** and **55**, for which other methods are without success. However, the recently reported[70] *syn*-1,6:7,12-bismethano[14]annulene **91** adds dicyanoacetylene in the wrong sense and does not provide the requisite progenitor for **54**.

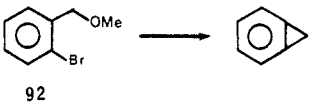


Even more recently, the use of the flash vacuum pyrolysis technique has provided access[71] to the hitherto unknown cyclopropa-*p*-benzoquinone. The molecule is very reactive and its existence as a reaction product was established from [$_{\pi}2 + _{\pi}4$] cycloaddition with anthracene.



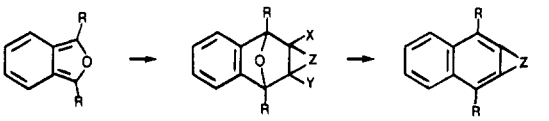
D. Miscellaneous Methods

The synthesis of cycloproparenes by 1,3-elimination between the α-position and an ortho position of a 1,2-disubstituted aromatic has obvious appeal because of its simplicity and the ready availability of requisite substrates. In 1974 Radlick and Crawford[72] reported that such a procedure gave **1** in 30% yield upon lithiation of **92**. However, attempted extensions of the work to the mono- and bisannelated homologues have



been unsuccessful[73] as have variations in the leaving group.[74] The sole successful application[75] of the method thus far reported pertains to the synthesis of **40a** in 5% yield from 4-bromo-5-(methoxymethyl)-1*H*-cyclobutabenzene. By comparison, the corresponding angular isomer **41a** has not been isolated from analogous cyclization, but its involvement as a reaction intermediate has not been discounted.[76]

One of the early schemes devised for the synthesis of cycloproparenes involved[77] attempted dehydration of **93a**. More recently, a similar sequence was applied[78]

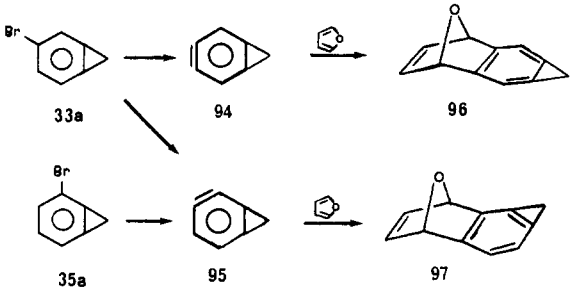


to the aza-substituted system **93b**. While unsuccessful in themselves (only products of three-membered-ring cleavage were isolated), a variation upon these procedures has been devised by Müller.[79] Thus the easily available benzofuran **93c** is aromatized in 72% yield when treated with low-valent titanium ($TiCl_3/LiAlH_4$). By comparison **93d** gives cyclopropa[*b*]naphthalene (**36**) in 45% yield together with 2-methylnaphthalene. This last compound does not arise from subsequent reaction of **36**. Analogous studies with simple furan adducts give cyclopropabenzenes mixed with alkylbenzenes, and the reaction sequence appears to have limited application.

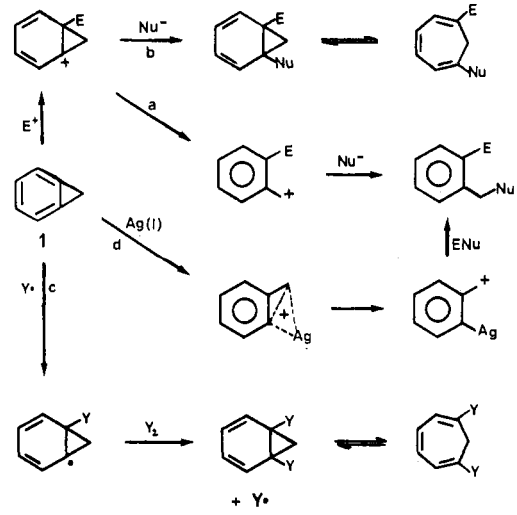
III. Reactions of the Cycloproparenes

The chemical reactivity of the cycloproparenes is markedly influenced by the strain energy (68 kcal/mol) of the ring system. Both theory[80] and experiment[81] agree that the HOMO of **1**, b_1, is located at the bridge (C1a–C5a) and the C3–C4 bonds and is higher in energy than the a_2 orbital. Thus **1** should react with electrophiles and in cycloadditions at the bridge bond, thereby relieving strain. While such reactivity has been used to advantage in recent times, reactions in which the bicyclic ring system is retained now include the first examples of electrophilic aromatic substitution and the synthesis of alkylidenecycloproparenes via the cycloproparenyl anion.

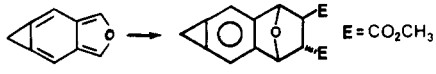
Retention of the cycloproparenyl framework is evident in the elimination–addition reactions of the 3- and 2-bromocyclopropabenzenes **33a** and **35a**. Upon



SCHEME XI



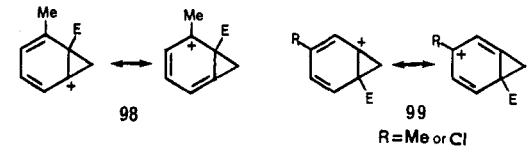
treatment with t-BuO^-/NH_2^- and in the presence of furan as trapping agent, adducts **96** and **97** are obtained.[82] The cyclopropabenzynes **94** and **95** must be formed as reactive molecules in solution. The distortions present in benzyne and cyclopropabenzene complement one another in **94** and account for the highly regioselective dehydrobromination of **33a** which leads to **96** and **97** in a ratio of ca. 98:2. The energy difference between **94** and **95** is calculated to be 2–3 kcal/mol, and this is consistent with the regioselectivity displayed; **95** is the most highly strained benzyne thus far recorded.[83] Retention of the cyclopropabenzene framework is also evident[59] in the reactions of the furan and thiophene derivatives **71**. Furan **71a** adds dimethyl fumarate to



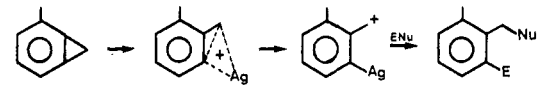
the four-electron furano moiety 4 times more slowly than isobenzofuran. This decreased reactivity could reflect a degree of reluctance on the part of the bismethylenecyclopropene to sustain increased π-character across the bridge bond.

A. With Electrophiles

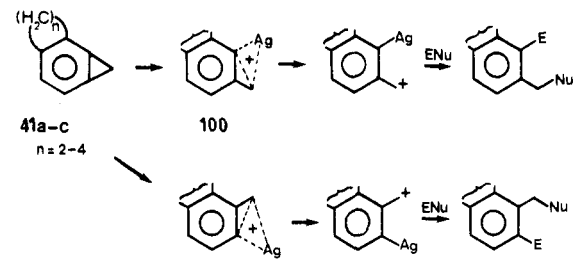
The behavior of the cyclopropabenzenes toward electrophiles is complicated by the facility with which opening of the three-membered ring occurs. For example, **1** and its derivatives react with acids[84] and with halogens[1,24,85,86] to give benzyl derivatives as the major reaction products. These results are best explained[80] by π-capture of the electrophile (E^+) at the bridge bond followed by disrotatory electrocyclic cleavage of the cyclopropyl cation thus formed (path a, Scheme XI). Subsequent interaction of the benzyl cation with the nucleophile accounts for the observed product. The regioselectivities observed with 3-chloro-[26] and 2- and 3-methylcyclopropabenzene[86] are consistent with this pathway whereby capture of the electrophile by the π-bond preferentially provides the more stable of the two cyclopropyl cations (Wheland intermediates). Thus the 2-methyl derivative gives meta-substituted xylenes via ion **98**, while the 3-isomer and the 3-chloro compound also give *m*-xylenes but via ion **99**. Furthermore, any capture of the cyclopropyl cation prior to ring opening will lead into the norcaradiene–cycloheptatriene manifold (path b, Scheme XI) as is observed[1,24] in the iodination of **1**; 1,6-diiodocycloheptatriene is formed as a minor product in yields of ≤7%. The formation of 1,6-disubstituted cycloheptatrienes dominates under photochemical conditions with fluorescent light (>400 nm). Thus the diiodo[24,70] and dithiocyanato[24] derivatives are formed from **1** in yields of 67 and 64%, respectively. In these cases, capture of radical at C1a and a radical chain mechanism giving norcaradiene (path c, Scheme XI) adequately account for the products.



The electrophilic cleavage of the three-membered ring of a cyclopropabenzene is mediated by metal ions, and the use of Ag(I) provides a highly effective method of benzylation. For example, the silver(I) ion catalyzed reactions of **1** with alcohols, amines, and thiols proceeds readily at 0 °C in aprotic media to give the corresponding benzyl derivatives in excellent yield.[5] The mechanism of these reactions most likely involves interaction of the metal ion with the strained σ-bond, followed by ring cleavage and nucleophilic capture of the benzyl cation thus formed (path d, Scheme XI). The various regioselectivities recorded[26,83,86] are usually *opposite* to those discussed above. Thus for 2-methylcyclopropabenzene the reaction yields *o*-xylenes



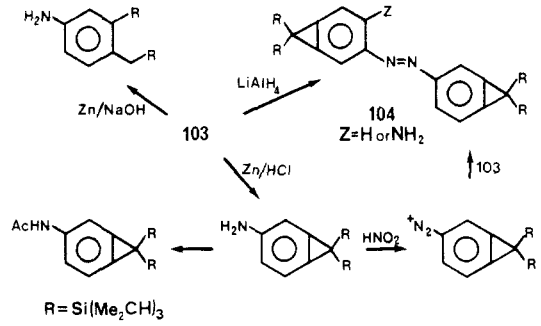
since the incipient ortho-substituted benzylic cation is the more stable. For the unsymmetrically ring annelated systems **41** the influence of additional strain is clearly important.[5,60] The Ag(I)-catalyzed reactions of **41a,b** are regiospecific and provide product via ion **100**,



whereas those of **41c** (whose strain energy is presumably very similar to that of **1**) show little selectivity; reactions with halogens show regioselectivity but in the opposite direction. It seems, therefore, that ions **100a,b** dominate from capture of the electrophile (Ag^+) by the σ-electrons. It is noteworthy that **41a,b** react with HCl in the *same* sense as with Ag(I), and one may speculate that the imposition of additional strain favors reaction with proton by the σ-route (path d, Scheme XI) over the π-route (paths a,b, Scheme XI).

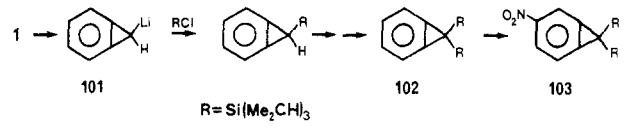
The use of silver(I) to promote the addition of alkenes, alkynes, allenes, and conjugated dienes to cyclopropabenzene[87] and the use of this ion, Cu(II), and Hg(II) in the dimerization of **1** have been reported upon[87,88] and discussed adequately elsewhere.[4,5] Suffice it to say that product formation is dictated by electrophilic addition of Ag(I) and subsequent interaction of the organosilver benzylic cation with the hydrocarbon

SCHEME XII



reagent to give ring-opened or ring-expanded products.

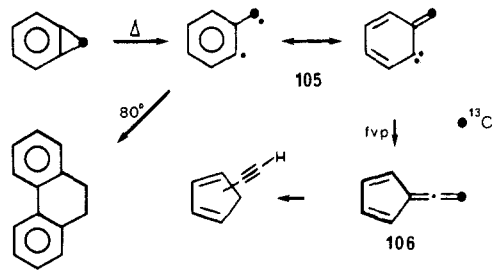
Theory[80] provides for electrophilic aromatic substitution of the cyclopropabenzenes without cleavage of the three-membered ring if the interaction of the electrophile with the HOMO occurs at C3(4). In order to promote such attack steric hindrance to interaction at C1a(5a) is necessary. This has been achieved[89] with bis(triisopropylsilyl)-1*H*-cyclopropabenzene (**102**), which



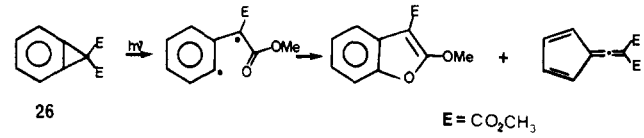
is obtained from **1** via the lithiated cyclopropabenzenyl anion **101** (see section IV.B). Treatment of **102** with 67% nitric acid under ultrasound conditions affords the 3-nitro derivative **103** (58%) in accord with the theoretical argument.[89] As yet no kinetic (or competitive) data are available to indicate whether **102** is nitrated more rapidly than benzene. In addition, the steric congestion present at C1 of **103** is sufficient to allow for its transformation into the range of derivatives shown in Scheme XII in which the three-membered ring is retained. Notable among these are the reduction to the 3-amino derivative (an unstable oil), its subsequent diazotization, and capture of the diazonium ion by **103** at the 4-position to give **104** (Z = NH_2).

B. Upon Thermolysis and Photolysis

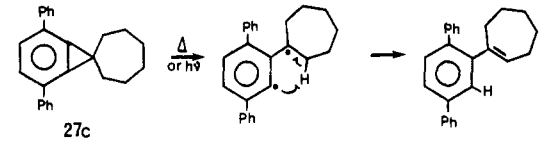
Vapor-phase thermolysis of cyclopropabenzene (**1**) at 80 °C results in dimerization and formation of 9,10-dihydrophenanthrene. Diradical **105** is implicated and



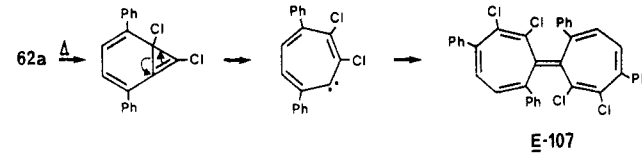
it has been diverted by reaction with buta-1,3-diene.[4,84] In the presence of radical initiators **1** is polymerized to poly(methylene-1,2-phenylene), and this product has now been shown to arise thermally but in lower yield.[90] Under flash vacuum pyrolytic conditions (>500 °C)[91] allene **106** is the major product, and it is formed without randomization of the carbon skeleton; Wolff-type rearrangement of the carbene form of **105** is most likely involved. Applied to cyclopropa[*b*]naphthalene (**36**), these conditions[91] provide 2-ethynylindene by H shift in the isobenzofulvenallene (cf. **106**). Species **105** is also a likely intermediate in the photolysis of **1** since the observed[92] dimerization to 9,10-dihydrophenanthrene and -anthracene is readily explained by head-to-head and head-to-tail coupling of this species. Furthermore, the involvement of **105** gains support from the isolation[93] of allene and furan products from photolysis of the diester **26**. The thermolyses of cycloproparenes



that carry a hydrogen atom on the α-position of the C1 substituent provide ring-opened styrene derivatives by hydrogen atom transfer through a five-membered transition structure, and a 1,3-diradical is again implicated.[18,94] For spirocycle **27c** kinetic measurements give[18] $\Delta G^{\ddagger}$ = 24.1 kcal/mol.



While the thermal dimerization of **1** and the rearrangement of **27** are comparatively straightforward processes, the dimerization of **62a** is more complex.

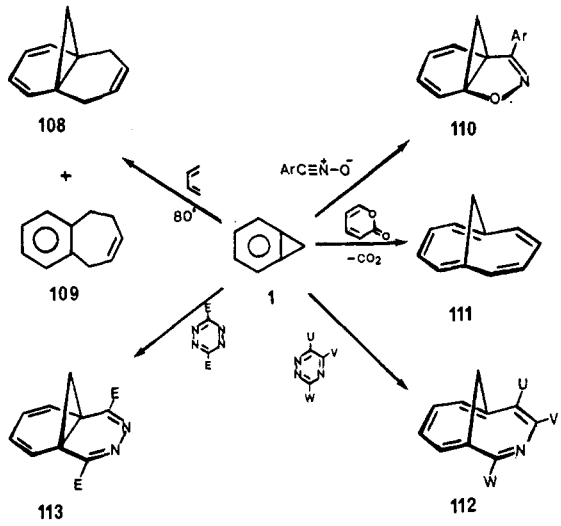


Mild thermolysis[95] of this compound results in the *E*/*Z* isomers of bicycloheptatrienylidene **107** (*E* isomer shown). Chlorine migration and ring expansion are involved, and the reaction appears to provide the only example of conversion from a bicyclo[4.1.0]hepta-1,3,5-triene to a bicyclo[4.1.0]hepta-2,4,6-triene; subsequent ring expansion to a cycloheptatrienylidene and coupling of the carbene with both modes of approach account for the products.[95]

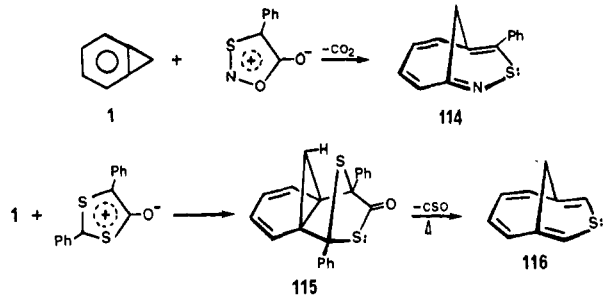
C. In Cycloadditions

The potential for cyclopropabenzene (**1**) to behave as a dienophile in Diels–Alder reactions was recognized soon after its initial synthesis and was brought to fruition[84] in 1968. As was discussed above, the HOMO of **1** is localized at the bridge bond, and thus the compound should behave[80] as an electron-rich olefin and propser in cycloadditions with inverse electron demand. Scheme XIII depicts a range of cycloadditions that exemplify the value of **1** in the synthesis of bridged annulenes. Thus **1** reacts with butadiene[84] to give the dihydro[10]annulene **108** in addition to **109**, the product of diradical trapping. It reacts with aryl nitrile oxides to yield the heterocyclic propellanes **110**,[96] with α-pyrone to give 1,6-methano[10]annulene **111**,[84] with 1,2,4-triazines to afford the 3,8-methanoaza[10]-annulenes **112** (several from reaction at high pressure),[97] and with 1,2,4,5-tetrazine-3,6-dicarboxylate to provide the diazotetraene **113**.[98] This last product[84] has now been isolated and characterized as the bisnorcaradiene[98] rather than its ring-opened valence bond isomer.

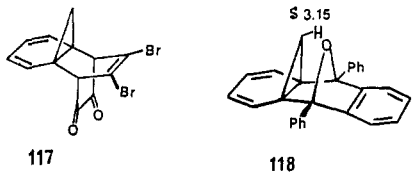
SCHEME XIII



Furthermore, bridged ten-electron [9]annulenes **114** and **116** emanate[99] from reaction of **1** with mesoionic oxathiazolines and dithiolanes, the latter via the isolable norcaradiene **115**.

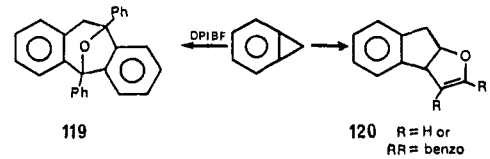


The formation of compounds **111–113** proceeds by way of thermally labile cycloadducts that undergo decarboxylation or deazetation under the reaction conditions. Consequently, the products provide no evidence for the stereochemistry of cycloaddition. By comparison, the addition of **1** to 4,5-dibromo-1,2-benzoquinone yields[100] **117**, the structure of which has

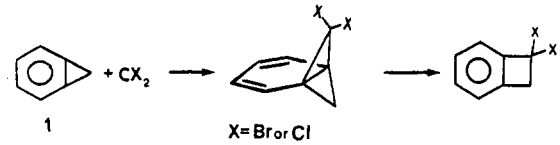


been determined by crystallographic methods.[101] This corresponds to exo addition of the diene component of the quinone to the bridge bond of **1** as required for a symmetry-allowed [$_\pi 6_s$ + $_\pi 4_s$] cycloaddition.[102] In contrast, the reactions between **1** and diphenylisobenzofuran[103] and diphenyldithiolene[99] afford the products of endo addition, namely, adducts **118** and **115**, respectively, and these formally correspond to [$_\pi 2_s$ + $_\pi 4_s$] processes. These last two compounds are assigned with the methylene and heteroatom bridges on the same face because of the significant deshielding experienced by the methylene hydrogen atom located syn with respect to the heteroatom (**115**, 3.58 ppm; **118**, 3.15 ppm). These data are more consistent with that for the cyclopropa[*l*]phenanthrene–furan adduct **87** (2.56 ppm) than that for its stereoisomer **88** (1.98 ppm).[68] Many cycloaddition reactions of cyclopropenes are influenced by steric factors[6,46,47] as discussed above, and it seems likely that these also dominate in the reactions of **1** through its bridge-localized HOMO. Thus the stereochemistry of adducts **115**, **117**, and **118** does not allow any conclusions to be drawn with regard to π-bond localization in **1**, viz., **1a** vs **1b**.

The behavior of **1** with diphenylisobenzofuran recorded above is at variance with that observed from reaction in chloroform at ambient temperature over 6 days.[104] Under these latter conditions Saito and his colleagues find that **1** gives rise to **119**. The structure



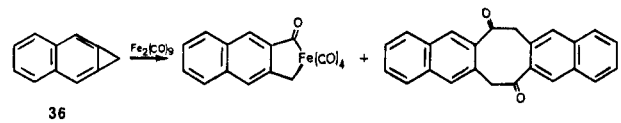
of the compound is assigned on the basis of magnetically nonequivalent methylene protons (3.17 and 3.75 ppm) and by comparison with the reactions of furan and benzofuran that lead to **120**. The absence of symmetry in adducts **120** excludes them as products of [$_\pi 2$ + $_\pi 4$] Diels–Alder cycloaddition across the bridge bond of **1**. Whether **119** and **120** are the thermodynamic products and arise by subsequent rearrangement of the Diels–Alder (kinetic) adducts or whether they are formed by capture of diradical **105** remains to be established. Similar ring expansion of cyclopropabenzene occurs upon addition of dihalocarbene. Thus reaction of **1** with dibromo- or dichlorocarbene (generated by the phase-transfer method) leads to the corresponding *gem*-dihalocyclobutarene in almost quantitative yield.[105]



Because 1,1-dibromocyclobutabenzene is also formed upon thermal carbene generation from phenyl(tribromomethyl)mercury and since radical traps are without effect, the direct involvement of the trihalomethyl anion and/or radical intermediates (cf. **105**) seems unlikely. It is tempting, therefore, to suggest that these products arise by way of a bicyclobutane intermediate as shown.

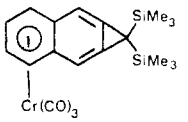
D. With Organometallic Reagents

Until a short time ago, the only known reaction between a cyclopropabenzene and an organometallic reagent was that of **36** with diiron nonacarbonyl as is depicted.[106] Since 1982 growing interest in the behavior of



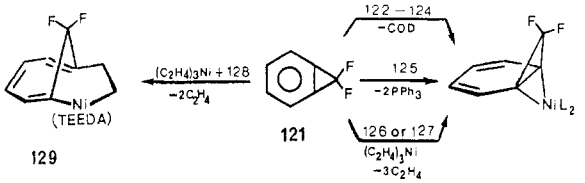
the cyclopropabenzenes toward organometallic reagents has culminated in the availability of products whose natures depend upon the metal–ligand combinations chosen. While attempts to form chromium sandwich compounds employing **1** have been unsuccessful,[107a] the complex [1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene]tricarbonylchromium has now been reported, but analogues from **1** or **36** (without silyl sub-

stituents) are not formed.[107b] Crystallographic data establish the structure as shown with an uncomplexed



cycloproparenyl moiety. Although only three other cyclopropabenzenes have been subjected to study thus far, there are similarities in their behavior with organometallics to the cycloadditions discussed above—metallobicyclobutanes and -cyclobutarenes are the most common reaction products formed.

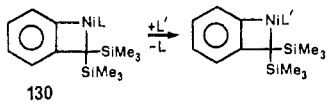
7,7-Difluorocyclopropabenzene[53] (**121**) reacts with the nickel(0) complexes **122–127** to give[108] nickelabicyclo-



122, $(Me_3P)_2Ni(COD)$ **123**, $(Et_3P)_2Ni(COD)$ **124**, (dcpe)Ni(COD) **125**, $(Ph_3P)_4Ni$ **126**, TMEDA **127**, bpy **128**, TEEDA

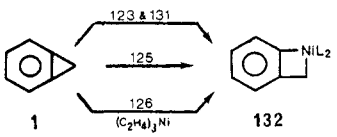
COP = cycloocta-1,5-diene;
dcpe = ethenebis(dicylohexyl)phosphine;
TMEDA = tetramethylethenediamine; bpy = 2,2′-bipyridyl;
TEEDA = tetraethylethenediamine

butanes in yields of 84–93%. These propellanes result from removal of olefin or phosphine ligands and addition of the metal across the cycloproparene bridge bond. The compounds, stable at ambient temperature, are oxygen sensitive and revert to **121** in solution at temperatures below −20 °C. If the reaction with tris(ethene)nickel(0) is performed in the presence of tetraethylethenediamine (**128**) rather than the tetramethyl homologue **126**, one ethene moiety is retained and the product[109] is the bridged nickelacyclononatriene **129**. In contrast to these reactions, 1,1-bis(trimethylsilyl)cyclopropabenzene[110] behaves in the *same* way with tris(ethene)nickel(0) and each of **126–128**, as well as with pentamethyldiethenetriamine, but gives[111] instead the ring-expanded nickelacyclobutabenzenes **130** (L =



130

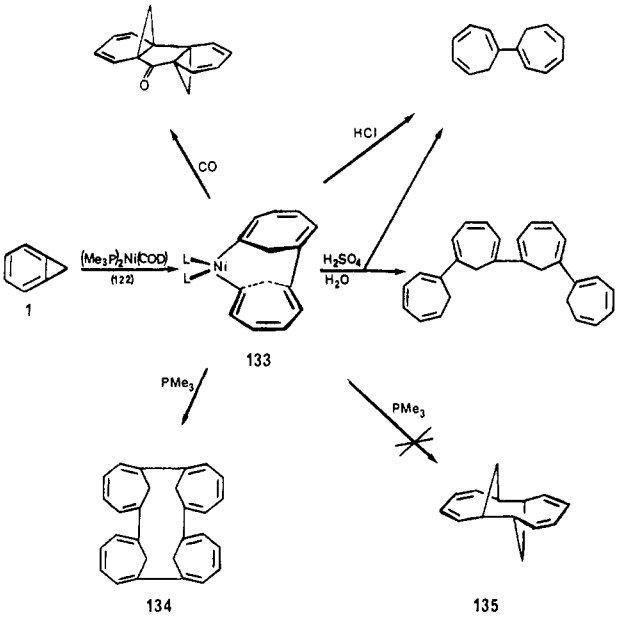
bidentate ligand) in 61–81% yield. Furthermore, ligand exchange can be effected in **130** by use of either phosphine or nitrogen donors, thereby expanding the available range of these unusual, and hitherto unknown, cyclobutarenes. Cyclopropabenzene itself reacts with **123**, **125**, **126**, and **131** in direct analogy with the behavior of its 1,1-bis(trimethylsilyl) derivative and gives nickelacyclobutabenzenes **132** and not bicyclobutane products.[112]



131 $(Bu_3P)_2Ni(COD)$

The formation of **130** and **132** formally involves the oxidative insertion of the nickel atom into one of the

SCHEME XIV

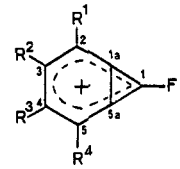


strained σ-bonds of the cycloproparene, and the reactions have analogy with the behavior of Ag(I) discussed earlier. The fact that **121** behaves differently and gives nickelabicyclobutane products suggests that the presence of a nonbonding electron pair on the cycloproparene 1-substituent is important. Indeed, stability could be gained by electron donation to the nickel atom and formation of a square-pyramid-like complex.[113] As with the carbene additions, it is possible that the nickelacyclobutarenes result from initial interaction of the Ni(0) complex with the cycloproparene HOMO; the nickelabicyclobutane thus formed is isolable only when further stabilization is possible.

Despite such possibilities, it has been found that the nature of the ligands has a dramatic effect upon the course of the organonickel reactions. Thus while **122** and **123** behave in the *same* way with **121**, compounds **126** and **128** do not. Moreover, the outcome of reaction between **1** and **122** (which contains trimethylphosphine ligands) is dramatically different from that with **123**, the triethyl homologue. The change to trimethylphosphine as the nickel ligand results in the oxidative addition of two molecules of **1** to the nickel complex with concomitant carbon–carbon bond formation and ejection of cycloocta-1,5-diene to give **133** (Scheme XIV).[114] Compound **133** is stable at room temperature under argon, and its Ni–C bonds have proved amenable to insertion reactions with subsequent reductive elimination of the metal. The fascinating range of compounds depicted in Scheme XIV is now available. Most notable among these is the tetramer **134**, a [24]-annulene, which is formed in preference to the expected dimer **135**; molecule **134** is not planar but cylindrical in shape.[114] The pathways of Scheme XIV further exemplify the potential utility of **1** in annulene synthesis.

The cyclopropabenzenes discussed above react both analogously and completely differently with (η^3-allyl)(η^5-cyclopentadienyl)palladium(III) in the presence of trimethylphosphine.[115] Thus *gem*-difluoride **121** gives a palladabicyclobutane, and 1,1-bis(trimethylsilyl)cyclopropabenzene a palladacyclobutabenzene with loss of the allyl and cyclopentadiene ligands. In contrast **1** affords the unusual and unexpected complex **136** in

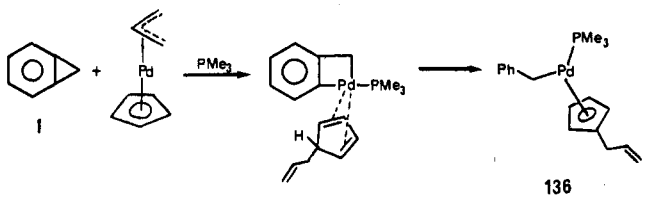
TABLE I. ^1H and ^{13}C NMR Parameters for Some 1-Fluorocyclopropabenzenyl Cations and Their *gem*-Difluoro Precursors[a]



compd	C1	C1a(5a)	C2(5)	C3(4)	H2(5)	H3(4)	ref
$R^1 = R^2 = R^3 = R^4 = H$ (**138**)	148.1	141.1	119.8	158.3	8.40	9.20	120–122
gem-difluoride (**121**)	100.3	129.5	116.0	134.7	7.45	7.45	121, 122
$R^1 = R^4 = H$; R^2R^3 = benzo fused (**139**)	148.0	129.1	119.6	153.6	~8.85		51
gem-difluoride (**65b**)	101.8	125.3	115.1	138.6	8.02		51
$R^3 = R^4 = H$; R^1R^2 = benzo fused (**140**)[b]					(7.98)	(9.43)	61
gem-difluoride (**74b**)[b]	101.7	129.4	120.6	136.9			
		(128.8)	(112.4)	(125.3)	(7.54)	(8.15)	61
$R^1 = R^4 = H$; R^2R^3 = naphtho[*b*] fused (**141**)							52
gem-difluoride (**66b**)	103.0	124.6	115.9	136.8	8.31		52
$R^1 = R^4 = H$; $R^2R^3 = CH_2CH_2$ (**142**)	145.1	138.8	110.7	183.2	8.04		50
gem-difluoride (**63c**)	101.6	127.0	109.6	154.2	7.14		50

[a] Chemical shifts in ppm downfield of TMS (δ = 0.00). [b] Values in parentheses are the chemical shifts of the parenthesized carbons.

79% yield, and a route via the palladacyclobutabenzene shown has been suggested.[115]



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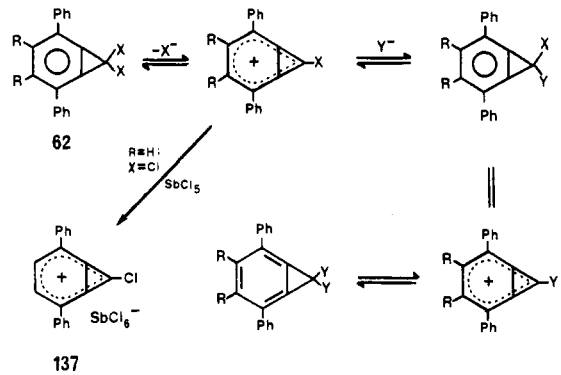
The behavior of other cyclopropabenzenes toward organometallic species has yet to be examined. Undoubtedly such studies will contribute significantly to the range of uses to which the cyclopropabenzenes can be put.

IV. Derivatives of the Cyclopropabenzenes

A. Cyclopropabenzenyl Cations, Anions, and Radicals

The existence of cyclopropabenzenyl cations (cf. **2**) has been adduced from their formation in solution under long-life conditions and from the isolation[116] of salt **137**. Earlier chemical evidence in support of cation



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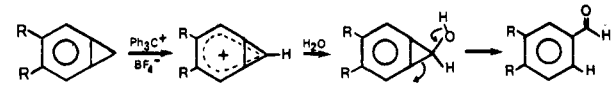
formation stemmed from a series of reactions in which the integrity of the cyclopropabenzenyl framework is maintained.[4] For example, the *gem*-dichlorocyclopropabenzenes **62a,d** undergo exchange of the halo substituents with hydride,[117] fluoride,[49,118] or carbanion reagents,[48,94] and in the case of **62b** fluoride ion exchange can be terminated[49] at the half-exchange stage to give **62c**. These reactions are best explained by ionization and subsequent nucleophilic capture of the cyclopropabenzenyl cation thus formed.

The exchange reactions are not restricted to functionalized cyclopropabenzenes as **1** and **36** both lose a hydride ion when allowed to react with trityl tetrafluoroborate.[119] The cyclopropabenzenyl cation so formed is captured by water, and the corresponding aryl aldehyde is the isolated product. The reaction with **1** is first order in substrate, and a deuterium isotope effect of 6.5 has been recorded.[119]



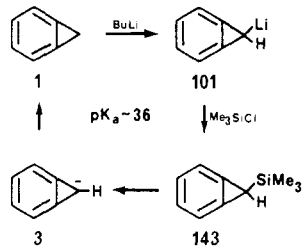
1 R = H

36 RR = benzo

In light of this chemistry it is hardly surprising that various *gem*-dihalocyclopropabenzenes have been ionized and the derived cations held under long-life conditions in solution for spectroscopic characterization.[50–52,61,116,120–122] For example, ionizations in fluorosulfonic acid at low temperatures have provided fluorocyclopropabenzenyl ions whose NMR spectral data are recorded in Table I. While the 1-fluorocyclopropabenzenyl[120,121] ion **138** (data confirmed from labeling studies[122]) and its -[*b*]naphthalenyl[51] homologue **139** have been fully characterized, the cyclopropa[*a*]naphthalenyl species **140** has lower stability and only ^1H and ^{19}F NMR data are available.[61] On the other hand, attempts to generate 1-fluorocyclopropa[*b*]anthracenyl cation **141** have thus far failed.[52] In this last case the tendency for protonation of the aromatic π-system is markedly enhanced, while at the same time the ion has the lowest localization energy (α_μ^+) at C1 of those shown in Table I; it is likely that protonation of the central aromatic ring dominates.[52] Ionization of *gem*-difluoro 3,4-ring-fused cyclopropabenzenes has also been effected[50] as exemplified by the most highly strained member, ion **142**. The shifts to lower field of the aromatic protons and carbons in the various cations compared with their precursors are fully consistent with related examples and with charge delocalization in the ions. The differences in the ^{13}C NMR shifts have been used to estimate the charge density distribution,[121] but it has been pointed out[123] that the Spiesecke–Schneider relationship[124] must be applied with caution; for cy-

clopropareny cations at least only a qualitative picture emerges. The relatively small change in the chemical shift(s) of C2(5) upon ionization implies that these centers carry very little charge in the ion. On the other hand, C1, C3, and C4 are significantly deshielded in the ions. At the time of writing neither **2** nor any other unsubstituted homologous cation has been characterized.

The fact that C1 of the 1*H*-cyclopropareneis is formally benzylic suggests that proton abstraction from the hydrocarbon should be possible and thus the existence of anion **3** plausible. Simple SCC–EH–MO



calculations[125] predict the cyclopropabenzenyl anion **3** to be less stable than cation **2** but nonetheless stabilized by electron delocalization. This would appear to be the case as **1** can be metalated at low temperature with butyllithium.[126] The organolithium **101** thus formed can be trapped with trimethylsilyl chloride to give silane **143**, and this is cleaved with sodium hydroxide some 64 times more rapidly than benzyltrimethylsilane.[126] The reaction with **143** exhibits first-order kinetics and anion **3** is undoubtedly involved. These data provide a pK_a of ca. 36 for **1**; toluene with a pK_a of 41 is less acidic. The results are supported by STO-3G calculations (pK_a calculated for **1**: 33),[127] which suggest that the C1–C1a(5a) bonds of **1** have a high polarizability. The large σ-charge placed at C1a and C5a is compensated for by the delocalization of π-charge away from these centers. It is this compensating π-delocalization that differentiates **3** from its cyclopropenyl anion equivalent, which is expected[127] to have a pK_a of 60. Despite the ease of metalation of the cyclopropareneis, there have been no spectroscopic studies of **3** or its derivatives reported. Nonetheless, the facility for anion formation has been utilized recently in the synthesis of a range of alkylidenecyclopropareneis **6** (see below).

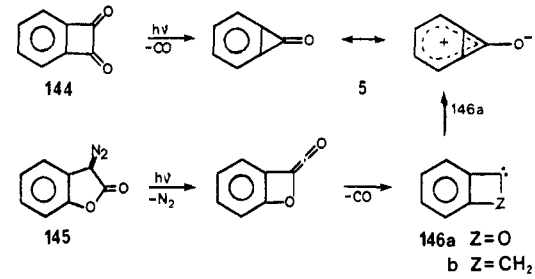
The cyclopropabenzenyl radical **4** is expected[125] to have a stability that lies somewhere between those of the (isolable) cation and the (observed) anion. However, attempted reactions with **1**, **36**, and even **62a** with suitable radical initiators have failed to provide any evidence for such species.[128] The preparation of more appropriate precursors for radical-induced decomposition thus remains a challenge.

B. Oxo- and Alkylidenecyclopropareneis

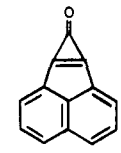
The existence of cyclopropareneones (1-oxocyclopareneis), e.g., **5**, as reactive molecules in solution was established almost 20 years ago.[129] The compounds are so sensitive to electrophiles and nucleophiles that isolation and characterization have been precluded.

However, low-temperature photolysis of **144** or **145** (Scheme XV) provides[130] small amounts of material at 8 K that exhibit a carbonyl stretching vibration at 1838 cm^{-1}. The compound is tentatively, but plausibly, assigned as ketone **5** since further photolysis results in

SCHEME XV

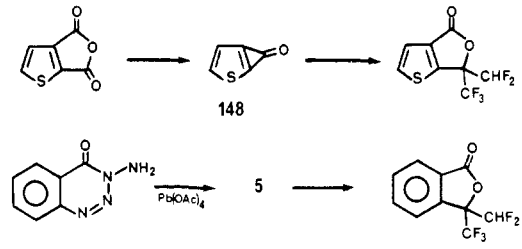


decarbonylation and the formation of benzyne. In this context it is noteworthy that the route to **5** from **145** most likely involves a Wolff-like rearrangement of carbene **146a**. By comparison carbene **146b** does not rearrange to methylenecyclopropabenzene.[131] Like **5**, ketone **147** has been isolated in a matrix prior to photodecarbonylation.[132]



147

The only recorded heteroatom cyclopropareneone is the thiophene derivative **148**. It is formed[133] upon flash



vacuum pyrolysis of thiophene-2,3-dicarboxylic acid anhydride and is trapped by pentafluoroacetone. Ketone **5** is similarly trapped and its formation here[133] and in other[134] flash vacuum pyrolysis studies parallels earlier work in which its involvement as a reaction intermediate was reasonably postulated.[4]

The discovery that diarylmethylenecyclopropareneis (cf. **6**) are surprisingly stable colored crystalline solids is recent[110,135] and is in marked contrast to their 1-oxo analogues discussed above. While stable derivatives of methylenecyclopropene have been known for 25 years,[136] the parent hydrocarbon has only recently been reported[137] and is unstable at temperatures above −75 °C. Similarly, the smallest parent radialene, trimethylenecyclopropane, polymerizes above 0 °C.[138] The alkylidenecyclopropareneis, e.g., **6**, combine into one molecule the features associated with both of these hydrocarbons. Thus they may be regarded as a cyclopropareneis **6a**, a benzannulated methylenecyclopropene

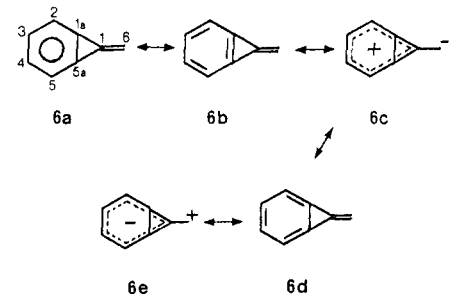
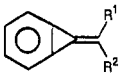
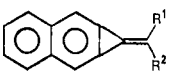


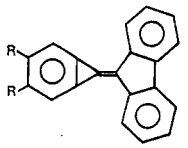
CHART IV



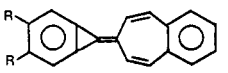
149a, $R^1 = R^2$ = Ph (38%, 1.0 D)[110,141]
b, $R^1 = R^2$ = *p*-$MeOC_6H_4$ (34%, 1.9 D)[110,141]
c, $R^1 = R^2$ = *p*-$Me_2NC_6H_4$ (24%, 2.2 D)[139]
d, $R^1 = R^2$ = *p*-$Me_3N^+C_6H_4I^-$ (61%)[139]
e, R^1 = H; R^2 = Ph (33%)[110]
f, R^1 = H; R^2 = Ph (33%)[110]
f, R^1 = H; R^2 = *p*-$MeOC_6H_4$ (31%)[110]
g, R^1 = Ph; R^2 = Me (10%)[110]



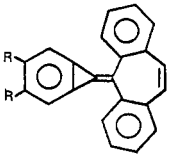
150a, $R^1 = R^2$ = Ph (90%, 0.4 D)[110,141]
b, $R^1 = R^2$ = *p*-$MeOC_6H_4$ (64%, 2.4 D)[110,141]
c, $R^1 = R^2$ = *p*-$Me_2NC_6H_4$ (55%, 3.0 D)[139]
d, $R^1 = R^2$ = *p*-$Me_3N^+C_6H_4I^-$ (62%)[139]
e, R^1 = H; R^2 = Ph (68%)[110]
f, R^1 = H; R^2 = *p*-$MeOC_6H_4$ (52%, 1.4 D)[110,141]
g, R^1 = H; R^2 = *p*-$Me_2NC_6H_4$ (94%, 1.8 D)[145]
h, R^1 = H; R^2 = *t*-Bu (68%)[110]
i, R^1 = Ph; R^2 = Me (42%)[110]



151a, R = H (22%, 2.6 D)[140,141]
b, RR = benzo (96%)[140,141]



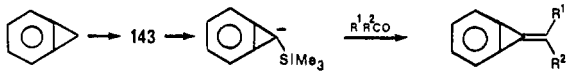
152a, R = H (9%)[140,141]
b, RR = benzo (57%)[140,141]



153a, R = H (11%, 1.2 D)[140,141]
b, RR = benzo (51%)[140,141]

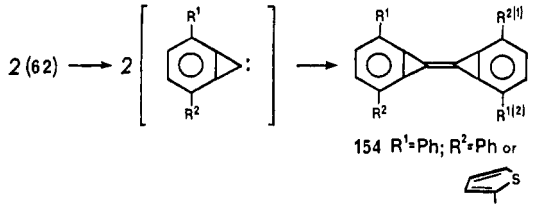
6b, a benzannulated triafulvene **6b–6c**, an unusual radialene **6d**, and an inversely polarized fulvene **6d–6e** all in one. Derivatives with polarities as depicted by **6c** and **6e** are now known, and the cyclopropareneparenyl moiety is established as an amphibilic entity.[139] The alkylidenecyclopropareneparenes have been the subject of a recent account,[135] and consequently only a brief synopsis of the pioneering work[110] is included here. However, developments recorded since the account was published are discussed.

Alkylidenecyclopropareneparenes are available by two routes. The more general of these[110,140,141] involves si-



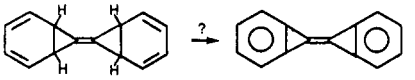
1 149

lyl–Wittig olefination employing a cyclopropareneparenyl anion to give the range of compounds **149–153** shown in Chart IV. These include the triapentafulvalenes (calicenes) **151** and the triaheptafulvalenes **152** and **153**; the experimentally determined polarities[139,141] of the compounds are also provided where they are known. The second pathway involves dimerization of a cyclo-



154 R^1=Ph; R^2=Ph or

propareneparenylidene[142] to give the dibenzotriafulvalenes **154** and is more restrictive because the substrate must be capable of forming a carbene (carbenoid). For this reason *gem*-dichloro precursors, e.g., **62a**, have been employed since they undergo facile halogen–lithium exchange at low temperature.[142] At the time of writing neither route has provided unsubstituted derivatives and, other than the air-sensitive **150h**, simple alkyl analogues are unknown. However, the recent synthesis[143] of the bisnorcaradiene **155** may ultimately provide access to **156**.



155 156

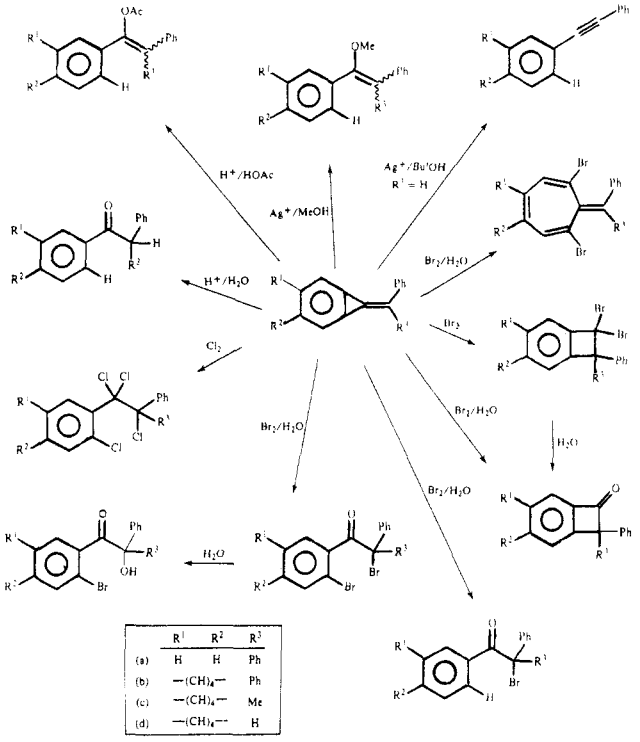
The available alkylidenecyclopropareneparenes are colored crystalline solids and provide the first examples of stable hydrocarbons to contain the methylenecyclopropene/trimethylenecyclopropane moieties. Of fundamental importance in the study of these compounds is the nature of the bonding and the presence or absence of charge separation (cf. **6b–e**). The expectation[136] of polarity in the alkylidenecyclopropareneparenes, and in particular in the fulvalenes **151–153**, is supported by ab initio molecular orbital calculations.[144] Thus while **1** should have a negligible dipole moment, **6** should have polarity as depicted by **6c** with a dipole moment of 1.49 D and the compound is expected to be less strained than **1** by ca. 3 kcal/mol. As can be seen from the data provided in Chart IV compounds **149–153** are polar (or capable of polarization) with dipole moments in the range 0.5–3.0 D, and their infrared (1765–1790 and 1510–1550 cm^{-1}) and ultraviolet (5–7-nm hypsochromic solvent shifts in polar media) absorption characteristics support this.[135] More importantly, the polarity displayed by the benzocalicene **151a** (μ = 2.6 D) and the fulvalene **149c** (μ = 2.2 D) reflect ambiphilicity in the cyclopropareneparenyl moiety.[139] The stabilization of both positive and negative charge must occur as illustrated by the structures **157** and **158** since these contain a

3.28 D

157 158

cyclopentadienyl "electron sink" and a *p*-dimethylanilino "electron source", respectively; calculations give **157** a dipole moment of 3.28 D in the direction shown.[144] Triaheptafulvalene **153a** (μ = 1.2 D) might be thought to be polarized in the same sense as **158**. However, calculations for the parent member of this system give

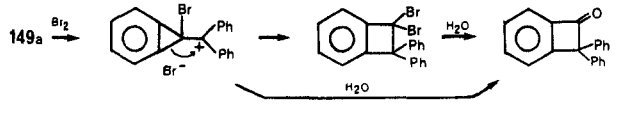
SCHEME XVI



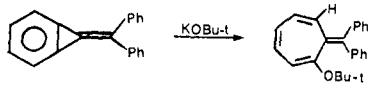
	R^1	R^2	R^3
(a)	H	H	Ph
(b)	$-(CH)_4-$		Ph
(c)	$-(CH)_4-$		Me
(d)	$-(CH)_4-$		H

a dipole of 1.12 D, with the cycloheptatrienylidene moiety as the negative end of the dipole,[144] viz., as in **157**. This is in no way untoward and suggests that the seven-membered ring of **153** is nonplanar.[135] Apart from their long-wavelength absorption maxima, several of the alkylidenecyclopropanes are fluorescent. Of particular interest is the fact that absolute fluorescence spectra reveal **150g** to have a quantum yield (Y_F) of 0.96 and be more fluorescent than fluorescein (pH 12, NaOH: Y_F = 0.91).[145]

The behavior of the alkylidenecyclopropanes toward electrophiles,[146] nucleophiles, and oxidizing agents[147] has been examined. As occurs with the simple cyclopropanes the chemistry of the alkylidene derivatives is also dominated by reactions that open the three-membered ring; a representative range of electrophilic processes is depicted in Scheme XVI. In each case examined the reaction is rapid and the electrophile is captured at the exocyclic carbon center. The ensuing cyclopropanyl cation is stabilized by one of a number of routes available to it. Of these the ring expansion to cyclobutarenes is notable[146] and involves addition/ionization as shown for **149a**. By comparison the re-

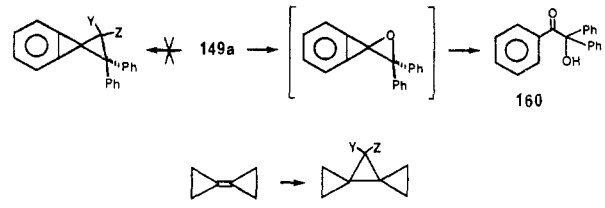


actions with nucleophiles are markedly slower[147] and then involve addition across the C1a–C5a bridge bond to give a heptafulvalene, e.g., **159**.

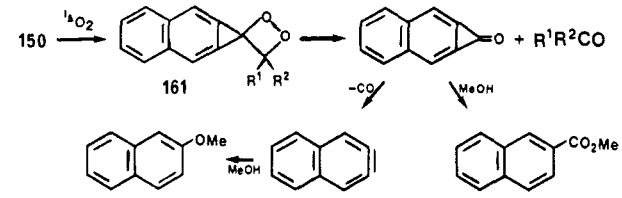


149 159

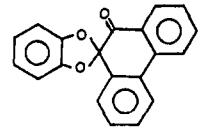
Peracid epoxidation of the exocyclic double bond of **149** and **150** appears to occur[147] as the oxidation leads to a hydroxyethanone, e.g., **160**. However, substrate



149 is resistant to the addition of carbene despite the use of conditions known to be effective with bicyclopropylidene. Upon singlet photooxygenation the alkylidenecyclopropanaphthalenes **150** give products



that not only suggest the involvement of dioxetane **161** but also provide definitive evidence[147] for the formation of cyclopropanaphthalenone. In particular, the partition of products to 2-methoxynaphthalene and methyl 2-naphthoate is the same irrespective of the exocyclic double-bond substituents (R^1 and R^2) present in **150**. The reaction with **149a** differs and results in a low yield of acetal **162**, which has been identified by X-ray methods.[148]



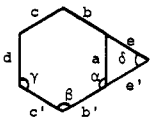
162

The diphenylmethylenecyclopropanes **149a**/**150a** each undergo reversible electrochemical reduction and oxidation to give a stable radical anion **163** and a quasi-stable radical cation **164**, respectively.[149] The anion

163 R=H or RR=benzo 164

radicals, formed by simple one-electron transfer, are particularly stable but react rapidly with oxygen when it is present. This reaction gives no new organic products but regenerates the alkylidenecyclopropane. The reversible formation of this species convincingly argues for retention of the ring system as depicted by **163** and **164**, and the electrochemical reductions occur (vs Ag/Ag^+: **149a**, −2.32 V; **150a**, −1.93 V) at *less* negative potentials than for many other aromatic hydrocarbons. The quasi-stable radical cations, each capable of further electrooxidation to a very short-lived dication, have half-wave potentials ($E_{1/2}^{\bullet+}$) for the initial oxidation step (**149a**, +0.68 V; **150a**, +0.81 V) that are less positive than for many other aromatic hydrocarbons in the same solvent. However, the higher value recorded for **150a** is contrary to the expectation that the more delocalized system should be more easily oxidized. The photoelectron spectra of these two compounds[150] reveal first ionization potentials that are fortuitously nearly equal (7.15 eV), showing that the observed differences in $E_{1/2}^{\bullet+}$ in solution has no clear counterpart in the gas phase. The solution-phase difference most likely results

TABLE II. Calculated and Experimental Geometries of Cyclopropabenzene (1) and Cyclopropa[*b*]naphthalene (36)[a]



compd	method	a	b (b′)	c (c′)	d	e (e′)	α (α′)	β (β′)	γ (γ′)	δ	ref
1	X-ray	1.334	1.367 (1.360)	1.382 (1.391)	1.390	1.498 (1.499)	124.8 (124.1)	113.1 (113.3)	122.3 (122.5)	52.9	160
	3-21G*	1.333	1.372	1.400	1.396	1.495	124.7	113.1	122.4	52.9	80
	VB-SCF	1.342	1.365	1.407	1.392	1.496	125.0	112.5	122.6	53.3	155
	FF-SCF	1.333	1.385	1.406	1.423	1.555	127.2	108.5	124.3	50.8	156
	MNDO	1.427	1.361	1.441	1.398	1.499	124.1	113.2	122.7	56.8	80
	CNDO/2	1.420	1.365	1.400	1.382	1.458	122.6	114.8			154
	MINDO/3	1.453	1.377	1.429	1.399	1.497	122.2	115.7	122.7	56.6	80
36	X-ray	1.368	1.337	1.437	1.439	1.504	124.9	114.7	120.5	54.1	2
	FF-SCF	1.349	1.367	1.437	1.449	1.556	128.0	108.7	123.4	51.4	156

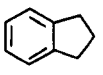
[a] Bond lengths are in angstroms and bond angles are in degrees.

from distinct structure-specific solvation energies in the radical cations **164**. The near identity of the first IPs also implies that the same fraction of charge should reside in the cyclopropareny component of each of the radical cations depicted by **164**. Thus on a per-atom basis the charge density in this component is lower in **164** (RR = benzo) because of the larger naphthalenyl moiety. Moreover, these data also imply that most (≈70%) of the charge resides on the Ph_2C unit in these gas-phase radical cations.

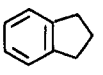
V. Physical and Theoretical Aspects of the Cyclopropareneses

The synthesis, characterization, and utilization of an ever-increasing range of cyclopropareneses continue to provide a stimulus to the practitioner at the bench. However, the technological advances that have facilitated detailed theoretical examinations in the area have had perhaps the greatest influence, not least because of the interactions between the experimentalist and the theoretician that these have brought.

Recent arguments have suggested that benzene is best represented as two equivalent Kekulé-type structures with alternating single bonds and bent, banana-like double bonds[151] and that a mixture of two resonating structures has a lower total energy than the time-honored Hückel model. Notwithstanding this, the concept of bond localization in the strained ortho-fused aromatics has continued to provide an arena for much debate.[152] The concept of aromatic bond localization was advanced in 1930 by Mills and Nixon[3] to explain certain differences in the chemical reactivities of indan and tetralin. Their postulate was that the strain in indan caused partial fixation of the aromatic double bonds in the direction indicated by **165a**. The experimental evidence upon which the hypothesis was based was subsequently shown to be erroneous. However, early extended-Hückel calculations[153] supported the concept in an *anti*-Mills–Nixon sense, with the favoring of **165b** over **165a**, and indicated that it should be more pronounced as the size of the ortho-fused ring decreases. Later semiempirical molecular orbital calculations[125,154] reversed this conclusion and suggested that in **1** structure **1a** is dominant.[4] More recent ab initio valence bond calculations[155] concur with the semiempirical approaches in predicting a significant Mills–Nixon effect in the direction of **1a**. On the other hand, ab initio molecular orbital calculations at various levels of theory lead to the expectation of a small effect only but in the *same* direction.[80]



165a

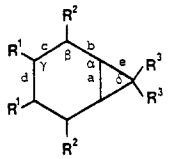


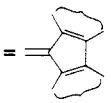
165b

Cyclopropabenzene (**1**) holds a crucial role in the bond fixation debate since it is the most strained of the ortho-fused aromatics and consequently the best candidate for exhibiting the phenomenon. Each of the calculations has provided a geometry for **1** that reflects distortions caused by the ring fusion. Without exception the semiempirical methods[80,154] lead to a bridge bond (bond a, Table II) that is long by comparison with benzene. On the other hand, the recent sophisticated calculations,[80,155] including force-field self-consistent field (FF-SCF) versions,[156] give to a value that is *shorter* than that of the benzene carbon–carbon bond. Furthermore, the C2–C3 bond (bond c, Table II) is usually long by semiempirical methods. Although the structures of cyclopropa[*b*]naphthalene (**36**)[2] and several cyclopropabenzene derivatives[157–159] have been reported and discussed,[4,5] the structure of parent **1** has now been accurately determined by Boese and his colleagues,[160] following crystal growth at low temperature in the X-ray diffractometer.[161] It is clear from the data of Table II that only the sophisticated ab initio calculations reproduce the geometry of **1** in an acceptable manner. The observed short bridge bond is reliably reproduced, and the trends and variations in the remaining bond lengths and interbond angles match the experimental results, with the 3-21G* calculations[80] providing the best fit. As noted with cyclopropabenzene (**1**), the FF-SCF calculations[156] give the correct trends in the cyclopropa[*b*]naphthalene (**36**) geometry but do not reproduce it particularly well.

The measured geometrical parameters for **1**,[160] **36**,[2] and several other derivatives[160,162–164] (including some alkylidenecyclopropareneses[110,164]) are collected in Table III. The standard deviations recorded permit an analysis of the bond lengths of the fused benzene ring. It should be noted that the earlier (less accurate) published structures[157,158] are not reproduced here and that the accurate low-temperature (120 K) X-ray results for **121** differ from the earlier microwave structure.[159] The important conclusion to be drawn from these data is

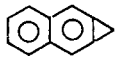
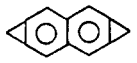
TABLE III. Structural Parameters of Some Cycloproparenes[a]



compd	substituents	a	b	c	d	e	α	β	γ	δ	ref
1[b]	$R^1 = R^2 = R^3 = H$	1.334 (4)[f]	1.363 (3)	1.387 (4)	1.390 (5)	1.498 (3)	124.5 (2)	113.2 (2)	122.4 (2)	52.8 (2)	160
102[b]	$R^1 = R^2 = H$, $R^3 = Si(CHMe_2)_3$	1.336 (3)	1.361 (2)	1.401 (4)	1.379 (6)	1.541 (1)	124.6 (2)	112.9 (2)	122.4 (2)	51.4 (1)	160
62e	$R^1 = R^3 = H$, $R^2 = Ph$	1.340 (4)	1.378 (5)	1.411 (5)	1.394 (4)	1.512 (5)	125.6 (3)	111.0 (3)	123.3 (3)	52.6 (2)	163
121[b]	$R^1 = R^2 = H$, $R^3 = F$	1.360 (1)	1.391 (2)	1.387 (2)	1.415 (2)	1.448 (2)	124.3 (1)	112.7 (1)	123.0 (1)	56.0 (1)	162
40a[b]	$R^1R^1 = CH_2CH_2$, $R^3 = H$	1.349 (1)	1.385 (1)	1.405 (1)	1.402 (1)	1.508 (1)	126.3 (1)	109.2 (1)	124.4 (1)	53.2 (1)	162
149a[c]	$R^1 = R^2 = H$, $R^3R^3 = {=}CPh_2$	1.355 (4)	1.379 (6)	1.384 (6)	1.388 (6))	1.433 (7)	124.0 (3)	113.0 (4)	123.0 (4)	56.4 (2)	110
151a[b,d]	$R^1 = R^2 = H$, $R^3R^3 =$ 	1.377 (5)	1.385 (6)	1.393 (6)	1.410 (6)	1.441 (6)	123.7 (4)	113.5 (4)	122.7 (4)	57.1 (3)	164
36	R^1R^1 = benzo, $R^2 = R^3 = H$	1.368 (5)	1.337 (5)	1.437 (5)	1.439 (5)	1.504 (5)	124.9 (3)	114.7 (3)	120.5 (3)	54.1 (3)	2
150c[b,e]	R^1R^1 = benzo, $R^2 = H$, $R^3R^3 = {=}C(C_6H_4NMe_2\text{-}p)_2$	1.399 (3)	1.352 (4)	1.437 (8)	1.431 (4)	1.440 (5)	124.3 (2)	114.4 (2)	121.3 (3)	58.1 (2)	164

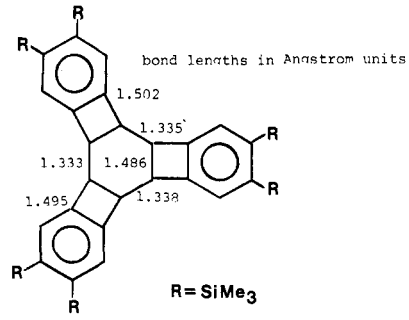
[a] Bond lengths are in angstroms and interbond angles are in degrees. [b] X-ray data recorded at 120 K. [c] $C{=}CPh_2$ = 1.343 (4) Å. [d] C=C = 1.338 (5) Å. [e] $C{=}CAr_2$ = 1.346 (3) Å. [f] Error in last digit.

TABLE IV. Heats of Formation and Strain Energies of Some Cycloproparenes

compd	strain energy,[a] kcal/mol	$\Delta H_f°$, kcal/mol	method	ref
	68		expt	2
	70	90	3-21G*	80
1	70	90	MNDO	80, 168
	67.8	104	expt	2
	69	105	MINDO/3	168
36				
	≥166		expt	5
	120	156	MINDO/3	168
38				
	140	164	3-21G	144
	139	159	MNDO	168
54				
	133	157	3-21G	144
	136	156	MNDO	168
55				
	207	227	MNDO RHF	32
	217	237	3-21G	144
56				
	170	190	3-21G*//3-21G	83
94				
	175	195	3-21G*//3-21G	83
95				

[a] Values are relative to the arene hydrocarbon.

that the geometries of the cycloproparenes are inconsistent with aromatic bond localization if alternating single- and double-bond character is to be judged from bond lengths. The experimental (and theoretical) results show that the cycloproparenes suffer markedly from bond length and interbond angle deformations while being almost planar—a tilt angle of 2–3° exists between the planes of the three- and six-membered rings. The deformations present are manifest in a shortening of bonds a and b (Tables II and III) compared with benzene (1.395 Å), while bonds c and d are similar in length to those of benzene. Nonetheless, bond a for the C1 sp^3 cycloproparenes (1.334–1.360 Å) is longer than that of cyclopropene (1.296 Å). These facts do not support a geometry that reflects either of the Kekulê structures **1a** or **1b**. Instead, the cyclopropparenes exhibit a reduction in symmetry, with deformations occurring as a result of the fusion strain.[160,165] Even the highly strained, bis-fused **40a** shows no bond length alternation. Rather, superimposition of the distortions present in both **1** and cyclobutabenzene[160] provides a molecule that has grown when compared with **1** and whose geometry[162] compares well with that calculated[83] for the linear benzyne **94**, where the strain energy is the sum of its two components. Thus bonds a, b, and c of **40a** (1.349, 1.385, and 1.405 Å, respectively) match their counterparts in **94** (1.350, 1.385, and 1.405 Å); bond d of **94** is shorter than that of **40a** as expected. To the best of our knowledge only one completely bond-localized aromatic structure has been recorded[166] and that is the tris(benzocyclobutadieno)-benzene **166**. The central benzene ring has alternating single- and double-bond lengths and internal angles close to 120°. The (arene)chromium complex formed with 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]-naphthalene apparently retains the characteristic features of the cycloproparenes in the uncomplexed part of the molecule.[107b] The bridge bond (bond a) at 1.384



166

Å is a little longer than that in **36** (1.368 Å).

Apeloig has pointed out[80] that the concept of bond fixation is concerned with the localization of electrons in the π-framework while the geometry is determined by π- and σ-effects. A theoretical index for probing the extent of any π-bond localization is the Milliken overlap population. The 3-21G values[80] computed for **1** when compared with the value for benzene point to a *small* bond localization in the direction of **1a** rather than the large effect[155] predicted from the VB-SCF calculations. The recorded[81] photoelectron spectrum of **1** indicates a substantial energy gap between the σ- and π-orbitals, and this is supported by the 3-21G calculations.[80] Thus the chemistry of **1** should be dominated by location of the highest occupied molecular orbital (HOMO) at the bridge (C1a–C5a) and the C3–C4 bonds. The fact that cycloaddition occurs across the bridge bond (section III.C) and that electrophilic aromatic substitution is at C3(4) (section III.A) is consistent with this. Moreover, if bond fixation is meaningful these results support it in the direction of **1b**! It must be concluded, therefore, that in terms of the structure, the chemistry, and the spectral properties of the cyclopropareneе, the concept of aromatic bond localization has little value.

The crystallographic data recorded in Table III include recently determined parameters for the alkylidenecyclopropareneе **149a**,[110] **150c**, and **151a**.[164] The effect of converting C1 from an sp^3 to an sp^2 center is to widen the C1aC1C5a angle (angle δ, Table III) by ca. 4° while contracting the remaining internal three-membered-ring angles by ca. 2°. The C1a–C5a bridge bond is lengthened by up to 0.04 Å, while the three-membered-ring σ-bonds are shortened by ca. 0.06 Å (see bonds a and e, Table III, respectively). The aromatic bonds attached to the fusion sites (bond b, Table III) are lengthened slightly (by ca. 0.02 Å) and the exocyclic double bond appears normal in length. The three-membered ring in these compounds is thus closer to an equilateral triangle than is the case for **1**. While this is consistent with the hybridization change at C1, it is also consistent with charge delocalization away from C1 as is expected from the known (Chart IV) polarity of these compounds. The experimental geometries are in good agreement with that calculated for **6** by ab initio methods at the 3-21G level. However, that of **151a** does not match that calculated by semiempirical methods.[167] These alkylidene derivatives are expected to be slightly less strained than their cyclopropareneе counterparts since the ab initio calculations give **6** a strain energy some 3 kcal/mol below that of **1**, viz., 67 kcal/mol.[144]

The deficiencies of the semiempirical molecular orbital calculations in predicting cyclopropareneе geometries are *not* reflected in the values computed for the heats of formation or the strain energies. Thus 3-21G* and MNDO calculations[80,168] agree in the value for the free energy of formation of **1** as ca. 90 kcal/mol. The strain energy of **1** has been measured[2] as 68 kcal/mol from the heats of silver(I)-catalyzed methanolysis reactions, and the theoretical models provide a reliable estimate of 70 kcal/mol (Table IV). The experimental value is ca. 15.6 kcal/mol greater than that for cyclopropene, and the difference reflects the increase in strain incurred in fusing the three-membered and benzene rings. The excellent agreement between experiment and theory allows use of the theoretical models as predictive tools for molecules whose strain energies have not been measured and for molecules yet to be synthesized. Strain energies and $\Delta H_f°$ values for a range of cyclopropareneе are collected in Table IV, and these show that cyclopropa[*b*]naphthalene (**36**) has a comparable strain energy to **1**. The effect of bis fusion as in **38** is to provide a shock-sensitive compound[30] that is calculated[168] to be somewhat less than twice as strained as **36**. However, unpublished[5] combustion data give **38** a minimum strain energy of 166 kcal/mol (clean combustion was difficult to achieve). Unless this value is the standard heat of formation, the discrepancy between theory and experiment is not easy to rationalize, particularly since the strain energy of dicyclopropabenzene **55** (133 kcal/mol) is calculated as essentially twice that of **1**. Despite this the data of Table IV do allow for comparisons to be made. Thus the reactive cyclopropabenzyne **94** is calculated to have a strain energy that is essentially the sum of the strains present in benzyne and **1**; the angular isomer **95**, though similar, is somewhat more strained (by ca. 3 kcal/mol).[83] The difference between **94** and **95** is also reflected in the as yet unknown[41,62] dicyclopropabenzenes **54** and **55**, where the angular isomer is expected to be the more strained by ca. 7 kcal/mol. It is interesting to note that the strain energies (and heats of formation) of these latter compounds are lower than those of the known[83] benzynes **94** and **95**, and thus there is no obvious (theoretical) impediment to their existence. The same cannot be said for tricyclopropabenzene **56**. The strain

56

167

energy of ca. 217 kcal/mol is likely to put it at or beyond the limit for detection. Dewar[39] has examined **56** and concludes that the activation barrier to conversion into cyclononatriyne (**167**) is a mere 7.9 kcal/mol.

As yet there are no estimates of the strain associated with cyclopropa[*a*]naphthalene (**48**), cyclopropa[*b*]-anthracene (**52**), or cyclopropa[*l*]phenanthrene (**85**). While **52** has moderate thermal stability,[37] there is a marked decrease in passing from **1** (which can be stored as a pentane solution at −10 °C for a period of months) to **85** (which is stable in solution at −60 °C for a period of hours only). Presumably the cyclopropareneе mirror their arene analogues to the extent that the π-character of the bridge bond increases in passing from the -benzene to the -[*a*]naphthalene to the -[*l*]phenanthrene derivative. On this basis the recorded decrease in stability through the series demonstrates a reluctance to sustain increased cyclopropene character in the three-membered ring. The behavior of the isobenzofuran

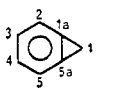
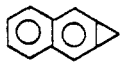
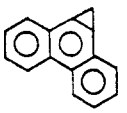
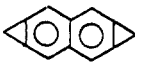
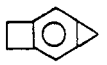
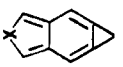
analogue **71a** with dienophile[59] is compatible with this explanation.

The NMR spectra of the cycloproparenes are fully compatible with species sustaining a diamagnetic ring current. The protons of the aromatic rings appear within the usual range, and their positions show that the ring current is not adversely affected by the distortions caused from ring fusion. For **1** the benzenoid protons appear as an AA'BB' system with H2(5) at 7.149 ppm and H3(4) at 7.189 ppm, respectively.[169] The methylene protons of **1** resonate at 3.11 ppm and all other cycloproparenes exhibit this signal in the range 3.0–3.6 ppm. It is worthy of mention that the variations in the position of this resonance in the naphthalene, anthracene, and phenanthrene derivatives (**36**, 3.40;[27] **48**, 3.42;[69] **52**, 3.56;[37] **85**, 3.54 ppm[67]) parallel those in the corresponding methylarenes. On the other hand, annelation of an alicyclic ring to **1** (cf. **40**, **41**, and **70**) causes only minimal change (3.05–3.18 ppm) from the position in **1**. Most notable among the ^{1}H NMR spectral parameters is the inverse value of J_{meta} (0.3–0.7 Hz) and J_{para} (ca. 1.9 Hz) for **1** and its derivatives when compared with normal aromatics.

The carbon-13 chemical shifts of the cycloproparenes reflect the unusual nature of the ring system.[4,5] Thus the carbon atoms adjacent to the sites of ring fusion [C2(5) in **1**] are shielded by comparison with the parent arene and the higher homologues. It should be remembered[4] that the original[170] assignments for **1**, cyclobutabenzene, and indan (**165**) have been revised[171] and that this shielding is most pronounced for the cycloproparenes (**1**, 114.7; cyclobutabenzene, 122.1; **165**, 124.7 ppm). Thus C2 of **1** and **36** is shielded by 13.8 and 15.7 ppm in comparison with benzene and C1 of naphthalene, respectively. In the simple cycloproparene hydrocarbons the C2 resonance is in the range 110–115 ppm (Table V), but the precise position is a function of the specific ring system present; cf. **71a**, 101.9 ppm.[59] This characteristic shielding may be regarded as diagnostic for the cycloproparenes. However, it is important to realize that the imposition of additional strain has a less recognizable effect. For example, in passing from benzene (128.5 ppm) to cyclobutabenzene (122.1 ppm), the ortho carbons are shielded by ca. 6.4 ppm, but in passing from **1** to **40a**, C2 is shielded by a further 3.6 ppm only. On the other hand, the benzenoid carbons of **71a,b** appear at 101.9 and 106.1 ppm, whereas they might be expected at 104.7 and 107.8 ppm, respectively, since C4 of isobenzofuran and isobenzothiophene resonate at 118.5 and 121.6 ppm, respectively.[59]

The influence of strain is also manifest in the magnitude of the one-bond C2–H coupling constants of the cycloproparenes. The value increases almost linearly from **165** (155.5 Hz) to **1** (168.5 Hz), and a value of ca. 170 Hz is characteristic for the series as the data of Table V show. Similar effects pertain to the magnitude of the C1–H coupling, but in this instance there is a marked increase (**165**, 127; **1**, 170 Hz) that reflects the cyclopropene (CH_2, 2.3 ppm; J_{C-H} = 167 Hz)[173] nature of the ring. Furthermore, the sites of ring fusion of **1**, C1a(5a), are shielded by comparison with the higher homologues (**165**, 144.0; cyclobutabenzene, 145.6 ppm), but in this case the special bonding of the cyclopropenyl moiety is responsible (cyclopropene HC=, 108.7 ppm); C1a(5a) resonate in the range 119–126 ppm. On the other hand, the remote C3(4) centers are essentially unaffected by ring fusion and the carbon resonances appear at similar chemical shift to their analogues in the parent aromatic hydrocarbon. One-bond ^{13}C–^{13}C coupling constants have been recorded[174] for **1**. Not surprisingly, the values for the C1–C1a and C1a–C2 bonds of **1** are anomalous by comparison with the higher homologues, but they are consistent with the Walsh model for cyclopropene.

TABLE V. ^{13}C NMR Assignments for Selected Cycloproparenes[a]

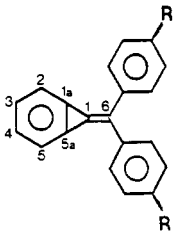
compd	C1	C1a(5a)	C2(5)	C3(4)	ref
 **1**	18.4 [170][b]	125.4	114.7 [168.5]	128.8 [159]	171
 **36**	18.6 [170]	123.4	112.3 [167]	136.7	171
 **85**	23.6 [171]	124.6 or 124.1	124.1 or 124.6	133.5	172
 **38**	19.9 [170]	122.8	113.5	140.1	30
 **40a**	19.2 [169.5]	122.8	111.0 [169]	145.5	33, 34
 **41a**	19.9 [170]	119.6 (126.0)[c]	135.9 (112.4) [166]	148.0 (121.0) [162]	34
 **71a**, X = O **b**, X = S	20.8 22.1	121.6 120.3	101.9 [171] 106.1 [172]	127.6 141.8	59

[a] Chemical shifts are in ppm downfield from internal Me_4Si. [b] Values in square brackets are the one-bond ^{13}C–H coupling constant in hertz. [c] Values in parentheses relate to the magnetically nonequivalent C5a, C5, and C4 atoms, respectively.

A rehybridization theory has been advanced[175] for the strained cycloalkabenzenes. The bridghead centers rehybridize and use orbitals with increased p character for bonding to the small ring. This leaves an orbital with enhanced s character for bonding to the adjacent ortho centers and results in an inductive polarization of the ortho-aromatic C–H bond. This is in accord with the higher field shift of C2(5), the increase in $^1J_{C(2)-H}$ and $^1J_{C(1)-H}$, and the ^{13}C–^{13}C couplings recorded.

The ^{1}H and ^{13}C NMR spectra of the alkylidenecycloproparenes **149–153** parallel those discussed above. The presence of the exocyclic double bond causes further shielding of the C2(5) centers (**1**, 114.7; **149a**, 111.0 ppm) as the data of Table VI show. More importantly, the remote electron-donating para substituents of the diarylmethylene moiety notably influence the chemical shifts of the cyclopropabenzenyl carbons; the effect is removed when mesomerism is no longer possible as in the quaternary ammonium salt **149d** (Table VI). These data support the results of dipole moment determinations which show that polarity increases in passing from **149a** to **149c** (Chart IV).

TABLE VI. ^{13}C NMR Assignments for Some (Diarylmethylene)cyclopropabenzenes[a]



compd	C1	C1a(5a)	C2(5)	C3(4)	C6	ref
R = H (**149a**)	112.8	131.5	111.0	134.2	109.9	110, 141
R = OMe (**149b**)	109.8	131.7	110.1	133.3	110.4	141
R = NMe_2 (**149c**)	108.0	130.1	108.9	132.4	111.6	139
R = $^+NMe_3I$ (**149d**)	115.9	130.7	112.2	135.8	105.6	139

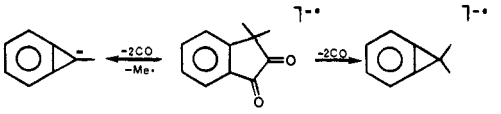
[a] Chemical shifts are in ppm downfield from Me_4Si as internal standard for DMSO-d_6 solutions.

The electronic absorption spectra of the simple cycloproparenes show that annelation of the three-membered ring to the benzene framework has little influence upon the aromatic chromophore.[4,5] Thus **1** [λ_{max} (cyclohexane) 252 (log ϵ 2.7), 258 (3.0), 264 (3.2), 270 (3.4), 277 nm (3.3)],[84] cyclobutabenzene, and *o*-xylene have similar ultraviolet spectra; the same is true of **36** and its derivatives when compared with their ring-opened dimethyl analogues. The influence of a second small ring upon the absorption maxima is notable. In the linear series **40a–c**, rocketene **40a** suffer a marked[4,5] bathochromic shift [λ_{max} (cyclohexane) 284 (log $\epsilon \approx 3.0$), 287.5 ($\approx$3.0), 294 nm ($\approx$2.8)][23] which is the largest in the series[5,60] and is also much greater than that previously[176] detected between dicyclobuta[*a*,*d*]benzene and durene. In contrast, an inverse effect is recorded[5] in the angularly fused isomers **41a–c**[60] whereby shifts to longer wavelength occur as the alicyclic ring size increases. These phenomena are compatible with the abilities of the alicyclic rings to be involved in hyperconjugation and with changes in the configurational composition of the lowest excited state.[4,5,177]

The UV spectra of the colored alkylidenecycloproparenes **149–153** show long-wavelength absorption maxima, the positions of which are solvent dependent in accord with the observed polarities.[139,141] Some of the compounds exhibit strong fluorescence as has been noted in section IV.B.

The infrared spectra of the cycloproparenes and their alkylidene derivatives are comparatively simple and reflect the symmetry of the systems. The parent series is characterized by a weak band at ca. 1675 cm^{-1} (**1**, 1662; **36**, 1673; **48**, 1687; **52**, 1678 cm^{-1}) due to the combination of a three-membered-ring skeletal vibration with the aromatic double-bond stretch. The alkylidene derivatives exhibit infrared absorptions in the ranges 1750–1790 and 1510–1550 cm^{-1}. These compare with 1810–1880 and 1510–1550 cm^{-1} for derivatives of methylenecyclopropene[136] and with 1770 and 1519 cm^{-1} for methylenecyclopropene itself.[137] These bands probably result from strong coupling between the exocyclic and endocyclic double bonds. The shift of the higher energy transition to lower wavenumber is consistent with dipolar structure. Indeed, it is noteworthy that the quaternary ammonium salts **149d** and **150d** show a marked increase in the intensity of the infrared combination band, which is also shifted from ca. 1750 to 1775 cm^{-1} by comparison with the mesomerically conjugated amine derivatives **149c** and **150c**, respectively.[139]

The majority of cycloproparenes provide a molecular ion in the electron impact mass spectrum, and the primary fragmentation is to the derived cycloproparenyl cation(s). Labeling studies have shown that the loss of a hydrogen atom from the molecular ion of a cycloproparene only occurs after complete scrambling and that the carbon atoms of **1** and **36** (at least) lose their positional identity prior to destruction of the ring system by loss of ethyne.[178] The alkylidene derivatives invariably show the molecular ion as the base peak of a simple spectrum.[110,141] The proposition of cycloproparenyl cations and radical cations as mass spectral fragmentation products continues.[179] Perhaps more important is the recorded fragmentation of radical anion **168** as this provides the first example of a cycloproparenyl anion and radical anion in negative-ion mass spectrometry.[180]



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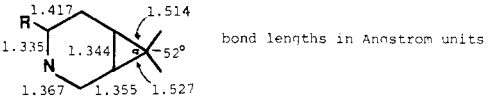
VI. Heteroatom and Related Derivatives

A. Heteroatom Derivatives

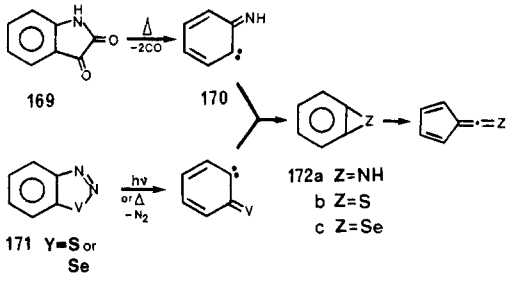
The synthesis of the cyclopropa[*c*]pyridine **19** (section II.B) has provided the first heteroatom cycloproparene.[16] The compound is a stable, crystalline solid when stored in an inert atmosphere, and its spectral properties are fully commensurate with its cycloproparene character. Ultraviolet absorption is recorded at 264 nm (cf. 3,4-dimethylpyridine, 267 nm), H2 and H5 resonated as doublets (J = 2 Hz) at 7.86 and 8.27 ppm, respectively, and C2 and C5 are shielded with resonances occurring at 130.75 (J_{C-H} = 189 Hz) and 101.39 ppm (J_{C-H} = 180 Hz), respectively; C2 is shielded by ca. 16 ppm. The crystallographic parameters are



19 R = PhCONH–

consistent with the carbocyclic analogues. Thus the bridge bond is similarly shortened to 1.344 Å while the C2–N3 distance is lengthened somewhat (1.367 Å) when compared with the (normal) N3–C4 distance of 1.335 Å; there is no bond length alternation. While there have been no estimates of the strain energy of this ring system, it is reasonable to presume a value comparable to that for **1** (68 kcal/mol). Moreover, the failure of the 3*H*-indazole route to provide the five-membered-ring homologues **23** undoubtedly reflects the requirements for 1,3-diradical cyclization rather than the strain associated with the tricyclic assembly.[17] The fact that cycloproparenes **40** and **41** have moderate thermal stability suggests that heteroatom equivalents should also be capable of existence, and syntheses of such compounds provide appropriate challenges for the future. With the exception of **19**, examples of methylene

SCHEME XVII



fusion across the ortho position of a heteroaromatic ring system are unknown.

In comparison to the above, heteroatom fusion across the ortho positions of the benzene ring has received both experimental and theoretical attention. Vapor-phase pyrolysis of isatin **169** results in bis-decarbonylation to **170**, and the involvement of aza-cycloproparene **172a** prior to ring contraction has been established from labeling studies (Scheme XVII).[181] In like manner, flash vacuum pyrolysis of the indazoles **171** leads to the thia and selena analogues **172b,c** as reaction intermediates.[182] By employing photochemical methods and matrix techniques Schweig[182] has isolated **172b,c**, and the compounds were found to display the characteristic infrared combination band at 1685 and 1672 cm^{-1}, respectively; upon further irradiation fulvenes are formed (Scheme XVII). The thermal decomposition of benzothiadiazoles, e.g., **171** (Y = S), does not always[183] give the thiacycloproparene, e.g., **172b**. However, with electron-withdrawing ester functionality located meta to the site of sulfur substitution, photolysis does give products via the intervention of the thiirene, e.g., **172b**. In thermal processes, reaction conditions are clearly important, and it is noteworthy that similar effects were recorded previously[4,184] in the behavior of benzotriazoles.

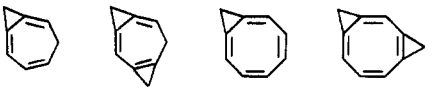
The oxygen atom is not expected to be an effective bridge for the ortho positions of an arene because of its smaller size and reduced polarizability compared to sulfur. The available evidence[4] suggests that the 1,2-ketocarbene equivalents to the intermediates of Scheme XVII do not interconvert via a 7-oxacyclopropabenzene. The sole theoretical study of heteroatom systems is at the SCF PPP level[185] and pertains to **172a** and the naphthalene homologues; the geometrical parameters, which include long bridge bonds, cannot be relied upon for the reasons outlined in section V.

B. Related Ring Systems

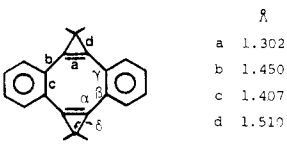
The fusion of a carbon atom across the sp^2 centers of unsaturated carbocycles other than the arenes is only now beginning to receive attention. For example, the only reported[133] case of fusion into a five-membered ring is the keto derivative **148**. The concept of fusion into

cyclopentadiene as in **173** and **174** is currently unknown. Of the two possible structures, **174** and its 3-heteroatom analogues are the most appealing and potentially most accessible.

In larger ring systems, the planarization of cycloheptatriene (cht) and cyclooctatetraene (cot) by cyclopropene fusion has been addressed[186] from the viewpoint of torsional strain. The barrier to ring inversion in cht and cot is sufficiently small (≤10 kcal/mol) to permit planarization by incorporating a fused three-membered ring as, e.g., in **175** and **177**, or perhaps

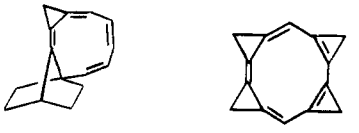


better by bis fusion as in **176** and **178** where the problems of bond shift isomerization are minimized. The only claim to a cyclopropacycloheptatriene appears to be for **179** but the structure assignment is not definitive.[187] That an eight-membered ring can be held planar and exhibit antiaromatic character has been established by Dürr and his group.[188] The dicyclopropacyclooctatetraene **180**, synthesized by the 3*H*-indazole route (section II.B), is planar with bond length alternation. MINDO/3 calculations[189] concur that the annelation of *all-cis*-cot with one or more three-membered rings will flatten the tub. Moreover, these data show that **177** ($\Delta H_f°$ = 87 kcal/mol) is more stable than its cyclopropene analogue by 6.8 kcal/mol while the dicyclopropa[*a*,*d*] structure **178** ($\Delta H_f°$ = 140 kcal/mol) is more stable than its dicyclopropa[*a*,*c*] isomer by 7.6 kcal/mol. The free energy of formation for the range of cyclopropanated cyclooctatetraenes has been determined[189] and tetracyclopropa[*a*,*c*,*e*,*g*]cycloocta-1,3,5,7-tetraene has the highest value, namely 216 kcal/mol. The planarization[186] of *all-cis*-cyclononatetraene and -cyclodecapentaene might be achieved with **181** and **182**, respectively.



179

180



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