Cycloproparenes

Brian Halton*

School of Chemical & Physical Sciences, Victoria University of Wellington, P. O. Box 600, Wellington, New Zealand

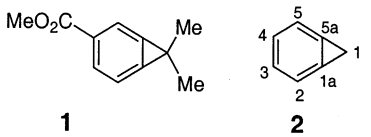
Received May 6, 2002

Contents

Brian Halton was born in Lancashire (England) in 1941. After college education in Lancashire and London, he studied at Southampton University and graduated with B.Sc. (Honors) in 1963. His Ph.D. was awarded in 1966 from the same institution for research performed under the direction of Professor Richard Cookson. Postdoctoral studies undertaken at the University of Florida with Merle Battiste were followed by a short period there as Assistant Professor. In late 1968, he transferred to Victoria University of Wellington and, in 1987, was awarded a D.Sc. from the university. Since 1991, he has held the position of Professor of Chemistry. He has received a variety of awards and recognitions that include the 2001 NZ Association of Scientists Shorland Medal, and Fellowship of the Royal Society of New Zealand (1992). He has served as President of the New Zealand Institute of Chemistry, is in his fourth term on its National Council, and is the NZ representative on the Pacifichem 2005 Organizing Committee. He has been a member of the International Advisory Boards of the former *Perkin 1* and *Perkin 2*, served two terms as the NZ member on the Advisory Board of the *Australian Journal of Chemistry,* and is currently Editor of *Chemistry in New Zealand*. He has spent periods of research and study leave as a Visiting Professor at a number of institutions in the US (Fulbright Scholar), the UK (British Council Scholar), Germany, Israel, Norway, and Australia. His research interests span the area of supranatural products with emphasis in the arena of strained organic molecules as illustrated by his editorship of the former JAI Press serial on the topic. Much of his research study has involved confrontation with the cycloproparenes.

I. Introduction

The field of the cycloproparene chemistry can be aptly regarded as something of a Cinderella area since the simple beginnings have led to a wealth of fascinating and fruitful chemistry far beyond expectation. Interest was initiated in the mid-1960s following the synthesis by Anet and Anet[1] of the first authenticated derivative, namely, ester **1**, that came from a 3*H*-indazole by way of photoinduced loss of dinitrogen and ring contraction (see path a, Scheme 1). After some 21 months, the preparation, isolation, and rudimentary properties of the highly odoriferous parent compound **2** were reported by Vogel, Grimme, and Korte.[2] These two communications clearly demonstrated that the fusion of a three-membered ring into the benzenoid framework was viable, thereby vindicating the ever-hopeful expectations of Perkin[3,4] almost 80 years earlier. Despite the clear demonstration that the class of compounds exists, Anet and Anet appear to have played no further part in evolving the area.



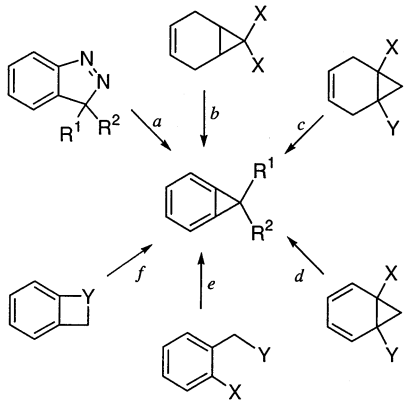
1 **2**

Claims to the synthesis of cycloproparene derivatives prior to the work of the 1960s had been made.

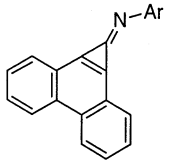
* E-mail: brian.halton@vuw.ac.nz; Ph: 64-4-463-5954; Fax: 64-4-463-5241.

10.1021/cr010009z CCC: $44.00
Published on Web 03/08/2003

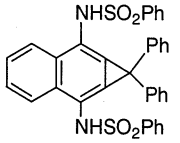
Scheme 1



De and Dutt[5] had suggested as early as 1930 that iminocyclopropa[*l*]phenanthrenes **3** could be formed, but the study subsequently was shown to be inconclusive.[6] Similarly, the work of Mustafa and Kamel[7] claiming *gem*-diarylcycloproparenes, e.g., **4**, while reproducible, gave products that were not aromatic as originally claimed.[8,9] These historical aspects of the field have been discussed in adequate detail earlier,[10,11] but when coupled with the prediction of Ullman and Buncel[12] that the strain energy of **2** should be some 45.5 kcal mol^{-1} above benzene, that the existence of stabilized C-1 cation, anion, and radical derivatives was predicted,[13] and that the C-1 cyclopropa[*l*]phenanthrenyl cation was a probable mass spectral fragmentation product,[14] the stage had been set for developments in cycloproparene chemistry.

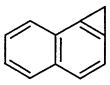


3

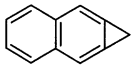


4

Since its inception, the chemistry of the cycloproparenes has attracted much attention and the field has seen reviews[10,11,15] and a chapter[4] as well as accounts on the alkylidene derivatives[16,17] from the present author. (Initially (and to some extent even today), the fusion of a three-membered ring into the benzenoid frame was declared informally to result in a *benzocyclopropene*. This nomenclature, while non-systematic, is straightforward and can be applied simply to higher members of the series such as the naphthalenes **5** and **6**. Prior to 1998, IUPAC rule A-21.3 required **2** to be defined formally as a 1*H*-bicyclo[4.1.0]hepta-1,3,5-triene but **6** (to which fusion nomenclature applied) as 1*H*-cyclopropa[*b*]naphthalene. Fortunately, a rationalization has taken place and since 1998 IUPAC recommendation FR-0 has placed "no restriction on when fusion nomenclature may be applied"; 1*H*-cyclopropabenzene is now as appropriate as 1*H*-cyclopropa[*b*]naphthalene and thus the correct terminology "*cycloproparene*" is used throughout this review. Additionally, IUPAC specify that the term "methylene" can apply only to a tetrahedrally bound CH_2 group. When reference to an exocyclic olefin is made, the general term is *alkylidene*, while that specific to the exocyclic >C═CH_2 moiety is *methylidene*. The chemistry of the alkylidenecycloproparenes is included herein.) Others have also provided an account,[18] a report,[19] book chapters,[20,21] and a micro review on nonbenzenoid cycloproparenes.[22] The present contribution encapsulates the recent studies into one place and offers not only critical yet comprehensive coverage from the time of the last *Chemical Reviews* but also indicates the likely direction of future studies. *Chemical Abstracts* has been searched with the aid of SciFinder Scholar 2000 through August 2002.



5



6

The strain energy of **2** has been calculated[23] as ca. 70 and measured[24] as 68 kcal mol^{-1}, and the magnitude approximates to this in all the known simple homologues. The juxtaposition of in-built strain and aromaticity has drawn much attention to the cycloproparenes over its 40-year history, both from a theoretical viewpoint and from independent experimental investigation. The laboratory practitioner needs to be ever vigilant as the volatile parent **2** and its crystalline higher homologues, e.g., **6**, are highly odoriferous. The thiol-like malodor of **2** is detectable at about 1 ppb such that the occasional laboratory misadventure, poor ventilation systems, and cracked or broken drainage pipes have provided fuel for conjecture; anecdotes sufficient for a winter evening's discourse have resulted. While issues of safety and toxicity have been raised—for alopecia in particular[25]—toxicological studies do not appear to have been performed, ostensibly because the odor was too severe for the facilities available. Clearly, workers in the area of cycloproparenes chemistry need to comply with the well-established principles of safe laboratory practice. In this context, it is noteworthy that none of the workers in our laboratories appear to have suffered ill effects.

II. Synthesis of the Cycloproparenes

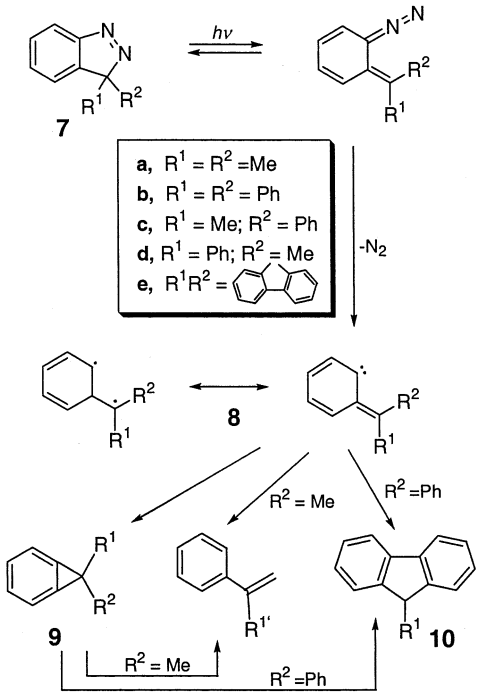
A variety of protocols exists that lead to the cycloproparenes in viable quantities, and these are displayed in Scheme 1. The high strain energy of the ring system limits the stability of the compounds such that decomposition above modest temperatures is common. Moreover, ring opening in the presence of electrophiles or transition metals is facile. In contrast, the cycloproparenes are stable to base, and so it is not surprising to find the majority of the procedures employ neutral or alkaline conditions, with base induced dehydrohalogenation providing the method of choice for synthesis. Formation of the ring skeleton prior to aromatization is most common, but it is not an essential feature of a synthetic protocol.

A. From Photolysis of 3*H*-Indazoles and 3*H*-Pyrazoles

As has been noted above, the first authenticated cycloproparene **1** was obtained from the ejection of

dinitrogen from a 3*H*-indazole upon photolysis.[1] The reaction has been the subject of more detailed examination in recent times.[26] Opening of the five-membered pyrazole moiety to give a diazo compound has been shown to precede photoinduced loss of dinitrogen that then delivers carbene, e.g., **8** (Scheme 2). Kirmse and co-workers[26] sought and obtained 1,1-

Scheme 2

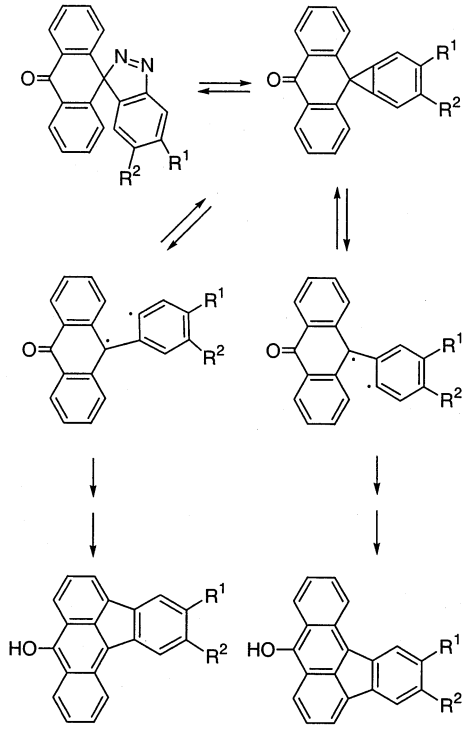


dimethylcyclopropabenzene (**9a**), but they were unable to isolate the aryl derivatives **9b**, **9c** (= **9d**), or **9e**. In protic media at least, carbenes **8a**−**e** are preferentially protonated, and the fate of the cationic intermediates derived from them was addressed.

The Kirmse study serves to remind us that 1- and 1,1-diarylcyclopropabenzenes, e.g., **9b**−**e** (Scheme 2), have yet to be isolated. Instead of these compounds, fluorene derivatives, e.g., **10**, are obtained and they can arise either directly from the diazo compound or from facile rearrangement of the arylcyclopropabenzene itself (see below).[27−29] In similar vein, attempts to obtain spiro-fused cyclopropabenzenes with the C-1 center spiro bound to a fluorene or an anthracene have also been examined.[30−32] Although no such derivative has yet been isolated, spirocyclopropabenzenes must be present as reaction intermediates because substituent scrambling is observed in appropriately labeled examples as illustrated in Scheme 3. The spirocyclopropabenzenes are more strained than simple diarylcyclopropabenzenes, and ring expansion takes place under the conditions of formation.

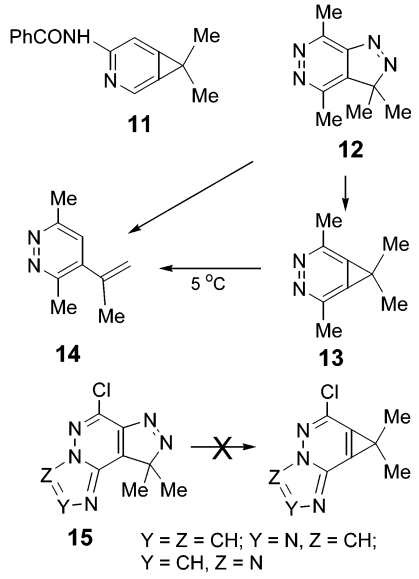
Despite the clear evidence for their intervention, none of the arylcyclopropabenzenes[27−32] have been the subject of examination at low temperatures. The use of glassy matrixes in the 3−10 K range could allow not only for their direct observation and characterization but also provide for analysis of the cyclopropabenzene−fluorene rearrangement. The trapping of transient cyclopropenes by Sander lends credence to such a proposal.[33]

Scheme 3



The generic deazetation sequence described above also provided **11** as the first[34] cyclopropapyridine in 1987. More recently,[35] the cyclopropapyridazine **13** likewise has been obtained (Scheme 4). Use of pyra-

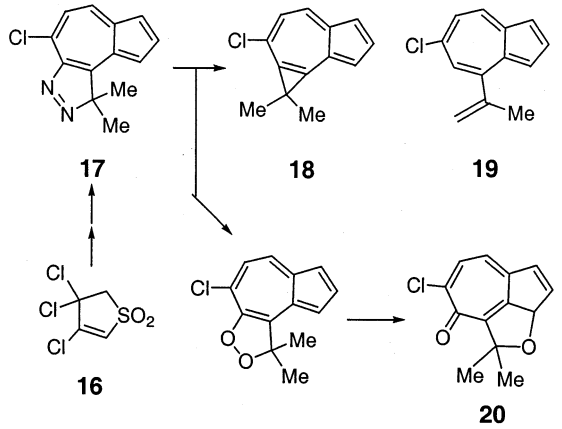
Scheme 4



zolopyradizine **12** served to confirm that the ring-opened diazo isomer is formed in cryogenic gas matrixes, but at 5 °C photolysis in pentane gives **13** as a somewhat unstable compound that isomerizes quantitatively to olefin **14** over a few hours at this temperature.[35] Despite this success, additional strain to the pyrazolopyradizine through fusion of a second five-membered ring, as for the heteroaromatic derivatives **15**, does not lead to successful closure upon nitrogen loss; the carbene/diradical intermediate was the only species intercepted.[36]

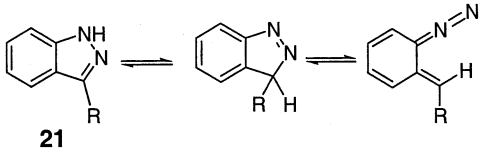
The most recent and interesting outcome of the pyrazole route has been in the isolation of the first nonbenzenoid cyclopropabenzene. Payne and Wege[37] prepared the azulenopyrazole **17** in four steps from the α,β-unsaturated sulfone **16**. Subsequent photolysis of **17** in ether at 0−5 °C gave the dimethylcyclopropa[*e*]azulene **18** in 46% yield (Scheme 5). In the

Scheme 5



presence of oxygen, interception of the diradical form of the intermediate leads to tropone **20** likely via the cyclic peroxide shown. Noteworthy here is that the alkene **19**, frequently the major product from deazetation of an indazole, is *not* formed, and geometric and/or conformational factors are suggested as responsible for this.[37]

Use of the spiropyrazole route to the cyclopropabenzenes as evolved by Dürr[38−41] has seen no developments since the 1988 clarification that the starting materials are not spiropyrazoles but 3*H*-indazoles,[42] and give cyclopropabenzenes as shown in Schemes 2−5. In addition, 3-monosubstituted indazoles preferentially exist in the 1*H*-tautomeric form, e.g., **21**. As yet there is no known example of a monosubstituted derivative undergoing tautomerism to its less favored form and then opening to the diazo isomer and ejecting dinitrogen.



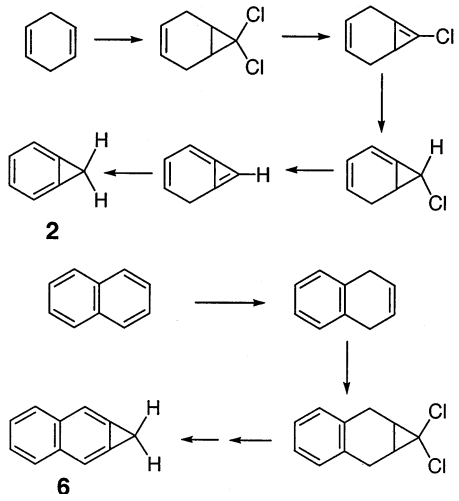
21

B. From Bicyclo[4.1.0]heptenes

1. By Employing 7,7-Dihalo Derivatives

The preparation of cyclopropabenzenes from 7,7-dihalobicyclo[4.1.0]heptenes (path *b*, Scheme 1) has provided a range of simple hydrocarbons from a sequence devised and executed by Billups and his students at Rice University. Cyclopropabenzene (**2**)[43,44] and cyclopropa[*b*]naphthalene (**6**)[45] are easily and conveniently prepared in acceptable yields. The reaction sequence involves the formation of a 7,7-dichlorobicyclo[4.1.0]heptene from addition of dichlorocarbene to an appropriate diene, followed by double dehydrochlorination (Scheme 6). The elimination sequence proceeds via a bicyclohept-1(7)-ene that

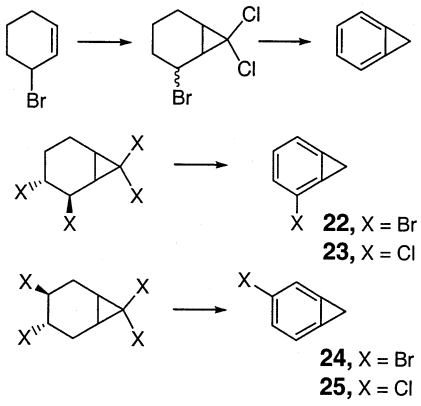
Scheme 6



undergoes prototropic shift with the double bond migrating from the more constrained cyclopropene into the six-membered ring. Its discrete existence has been demonstrated from interception by Diels−Alder cycloaddition.[46] A second elimination delivers the desired hydrocarbon in ca. 40% yield and C-1 labeling studies have shown that skeletal rearrangement is not involved.[47]

It must be noted that the cyclohexa-1,4-diene is not a critical substrate to **2** or its derivatives. The more easily available 1,3-isomer provides "angular" bicyclohept-2-ene upon dichlorocarbene addition and the double dehydrochlorination is effected with comparable efficiency.[48,49] Furthermore, Neidlein[50] has shown that 3-bromocyclohexene, the customary precursor to cyclohexa-1,3-diene, may be used directly as it adds dichlorocarbene and the resultant 3-bromo-7,7-dichlorobicyclo[4.1.0]heptane ejects both HBr and HCl on treatment with *tert*-BuOK to give **2** in 33% yield (Scheme 7). This protocol has advantage for the

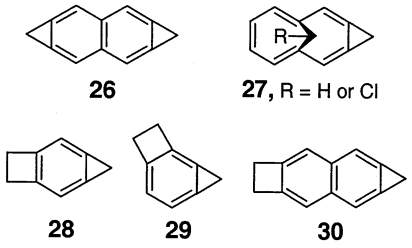
Scheme 7



synthesis of **2** since cyclohexene is more readily available than cyclohexadiene. In addition, the use of 2,3,7,7-[51,52] and 3,4,7,7-tetrahalobicyclo[4.1.0]-heptanes[51,53−55] also allow for such tris-eliminations giving rise to the exceptionally odoriferous 2- and 3-halocyclopropabenzenes **22**−**25** in comparable yields (Scheme 7).

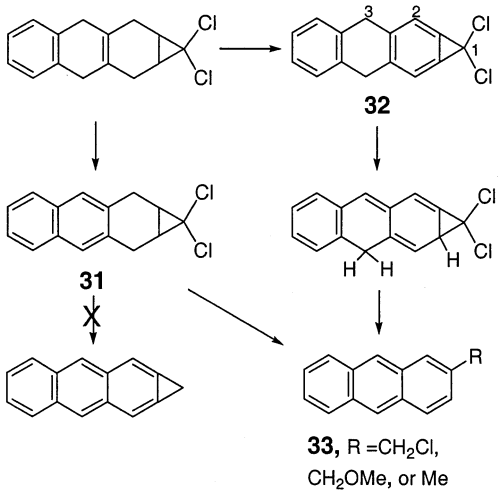
Apart from the fundamental hydrocarbon frameworks detailed above, the use of *gem*-dihalobicyclo-

heptenes has provided a range of novel cyclopropparene derivatives. Thus, dicyclopropa[*b*,*g*]naphthalene (**26**),[56,57] the cyclopropamethano[10]annulenes **27**,[58,59] and the cyclobutacyclopropabenzenes, "rocketene" **28**,[49,60] and its isomer **29**[49,61] have been prepared in fair yields. The naphthalene analogue of **28**, cyclobuta[*a*]cyclopropa[*f*]naphthalene (**30**) is more readily available by this procedure than others (see below).[49,62] In contrast, the provision of simple alkyl[63] and ether[64,65] substituted derivatives in the benzene and naphthalene series, respectively, by this protocol can be regarded as routine.



What need to be recognized are the limits to which the Billups route can be applied. When attempts are made to prepare cyclopropa[*b*]anthracene by double dehydrochlorination and aromatization of **31** only ring-opened anthracenes **33** (R = CH_2Cl or CH_2OMe) are obtained (Scheme 8).[62,63] Since the ether product

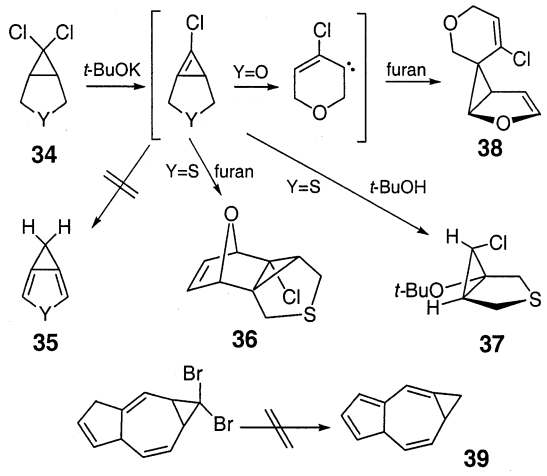
Scheme 8



is derived from the chloride, it is clear that aromatization with opening of the three-membered ring is preferred to formation of cyclopropanthracene. If the precursor to **31** is employed directly then 2-methylanthracene (**33**, R = Me) is the major product of reaction. It is presumed that the dihydrocyclopropparene **32** is formed but that it does not survive the basic reaction conditions. Likely, base induced proton shift from C-3 to C-1a triggers opening of the three-membered ring with aromatization upon removal of the remaining benzylic proton (Scheme 8). As no linear acene derivative with more than two aromatic rings, viz. cyclopropa[*b*]naphthalene (**6**), has been prepared by this route, one must conclude that the driving force for relocation of the initially formed cyclopropene double bond is no longer competitive with ring opening which takes place instead.

In directing attention toward the five-membered heteroaromatics, cyclopropa[*c*]furan (**35**, Y = O)[66,67] and cyclopropa[*c*]thiophene (**35**, Y = S)[68] (Scheme 9),

Scheme 9



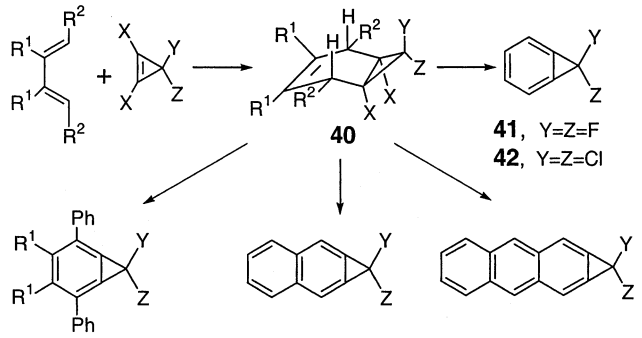
it was found that double dehydrochlorination of the bicyclo[3.1.0]hexane framework is thwarted and the desired cyclopropparenes are not isolated. The loss of HCl from **34** is recorded, but the fate of the resultant $\Delta^{1(6)}$-alkene is dependent upon the heteroatom present. Furan and *tert*-BuOH intercept the thiophene derivative as **36** and **37**, respectively, from addition across the π bond.[68] In contrast, the furan analogue (with the smaller heteroatom) is intercepted from Diels−Alder addition of its π bond with the more reactive diene, diphenylisobenzofuran (DPIBF), to give the analogue of **36**. In the presence of furan, ring expansion to a cyclohexenylcarbene takes place faster than trapping and spirocycle **38** is isolated (Scheme 9).[66,67] Fusion of a three-membered ring into a simple cycloheptatriene manifold to give a cyclopropacycloheptatriene has not proved easy,[22,69] although Payne and Wege have obtained **18** by the pyrazole deazetation route.[37] Most notable in the context of double dehydrohalogenation is the fact that cycloprop[*f*]-azulene (**39**) is not detected from the black insoluble product obtained from didehydrobromination of the precursor at −78 °C (Scheme 9).[22]

2. By Employing 1,6-Dihalo Derivatives

The formation of cyclopropparenes from use of an appropriate 1,6-disubstituted bicyclo[4.1.0]hept-3-ene (path *c*, Scheme 1) is comparatively easy. The use of a double dehydrohalogenation protocol requires abstraction of protons from C-2 and C-5 with sequential or concomitant loss of the bridge halogen atoms. This method has come to form the basis of modern cyclopropparene synthesis since the product is formed directly without need for a rearrangement step and yields are generally higher than from the *gem*-dichloro analogue. The elimination sequences follow the conventional requirement of antiperiplanar transition structures for bimolecular eliminations or the presence of stabilizing substituents at C-2/5 to facilitate E1-like processes. The requisite bicycloheptene is conveniently obtained from Diels−Alder cycloaddition of a 1,3-diene to a 1,2-dihalocyclopropene.

Initially, the configuration of such Diels−Alder adducts was presumed to result from compliance with the Alder *endo* rule.[70] However, it was shown subsequently that cyclopropenes which carry a bulky flagpole (C-3) substituent add instead from the *exo* face[71−73] to provide a substrate that carries an antiperiplanar proton and halogen atom as depicted by **40** in Scheme 10 (see below). In the early work,

Scheme 10

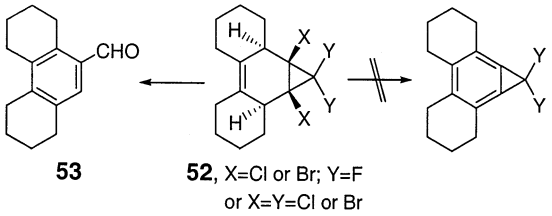


tetrahalocyclopropenes were used almost exclusively,[10,11,15] but the mid-1980s saw the development of a facile and straightforward synthesis of 1-bromo-2-chlorocyclopropene by Billups and co-workers.[74] This has been used to such an extent that the molecule has become the substrate of choice for 1*H*-cyclopropa**r**ene syntheses providing the requisite diene is available.[4,21]

(a) Derived from Tetrahalocyclopropenes. Some of the highest yielding syntheses of the cyclopropa**r**enes have come from the didehydrohalogenation of tetrahalocyclopropene adducts of buta-1,3-dienes as illustrated for dihalocyclopropa**r**enes **41**−**51** of Scheme 10. The reaction dates from 1968 when Vogel et al. appended this route (ca. 40%) as an alternative to the preparation of *gem*-difluorocyclopropabenzene (**41**) by flash vacuum pyrolysis.[75] This particular synthesis has been optimized and up to 50 g of product can be obtained from a didehydrochlorination that proceeds in 60% yield.[76] Use of tetrachlorocyclopropene and 1,4-diphenylbuta-1,3-diene provides the *gem*-dichlorocyclopropabenzene **43** from a dehydrochlorination that is essentially quantitative,[77,78] and the higher homologue **46** has been obtained from a simple extension of the process.[79,80]

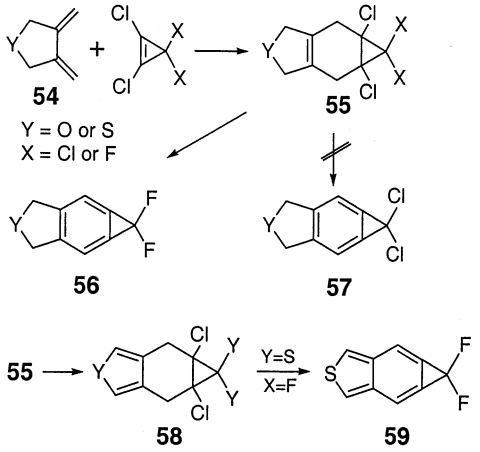
By employing less easily available dienes, Müller and his group have provided the naphthalenes **48** and **49**,[81,82] and the anthracene homologues **50** and **51**.[83−85] Moreover, as a method for preparing *gem*-difluorocyclopropa**r**enes this double dehydrochlorination protocol commencing with 1,2-dichloro-3,3-difluorocyclopropene is without precedent.[76,81−89]

Attempts to synthesize bis-fused cyclopropa**r**enes commencing from 1,1′-bicyclohexenyl and a tetrahalocyclopropene have not been successful. While the Diels−Alder additions take place to give **52**, subsequent reaction with strong base effects dehalogenation and not dehydrohalogenation;[90] aldehyde **53** that results is unlikely to be formed by way of the cyclopropa**r**ene. It would seem that the configuration of **52** should be as depicted resulting from *exo*-addition of the dienophile to the diene[71−73] rather than the *endo*-adduct assumed in the original publication.[90]



In contrast to the above, use of the heterocyclic exocyclic dienes **54** (Y = O or S) with tetrachloro- or dichlorodifluorocyclopropene afforded the "*exo*"-derivatives **55.** However, it is only the dichlorodifluoro derivatives that easily lose two molar equivalents of hydrogen chloride and give the isolable *gem*-difluorocyclopropabenzofuran and -thiophene derivatives **56** (Y = O, 43%; Y = S, 50%).[86] Müller has noted many times that 1,1-difluorocyclopropabenzenes are as easily isolable as the parent hydrocarbons, while the dichloro analogues are capable of isolation only in exceptional circumstances.[81,84,87,89,91] This certainly proved to be the case for the examples at hand as analogous treatment of the tetrachloro derivatives **55** (X = Cl) with strong base led to the isolation of uncharacterized decomposition products rather than **57**.[86] It is reasonable to assume that the sought after compounds are unstable to the reaction conditions essential for their formation. Dehydrogenation of the heterocyclic ring of **55** with DDQ affords the 6π electron tetrahaloheteroaromatics **58**, but it is only the dichlorodifluorothiophene derivative that transforms into an isolable 10π aromatic heterocycle as shown for **59** (Scheme 11); the cyclopropa[*f*]benzofu-

Scheme 11

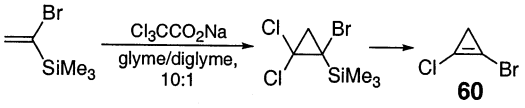


ran is not obtained.[86] More recently, Anthony and Wege[92] have prepared the parent members of this nonbenzenoid cyclopropa**r**ene series employing 1,6-dibromobicycloheptenes (see section IIB,2b).

The outcome of these and other studies suggests that there is interplay between the facility for dehydrohalogenation, the nature of the halogen to be lost, the conformational flexibility of the substrate, and the stability of the product to the conditions employed. Without doubt, the nature of the halogen atom(s) can play a crucial role as has been demonstrated for the 1,6-dihalobicycloheptenes.

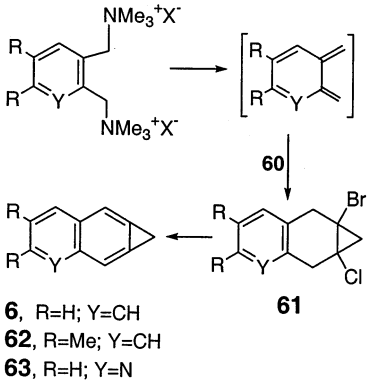
(b) Derived from 1,2-Dihalocyclopropenes. As was noted earlier, the group of Billups at Rice University has provided a straightforward synthesis of 1-bromo-2-chlorocyclopropene (**60**)[74] by addition of dichlorocarbene to α-bromovinyltrimethylsilane (Scheme 12).[93] A comparable synthesis of 1,2-dibromocyclopropene also has been reported,[94] but it is the former that behaves as the more efficient dienophile with hydrocarbon dienes. Thus, 1-bromo-6-chlorobicycloheptenes are more easily available than their 1,6-dibromo analogues and they have provided the wherewithal to produce a wide range of cyclopropa-arene-containing molecules.

Scheme 12



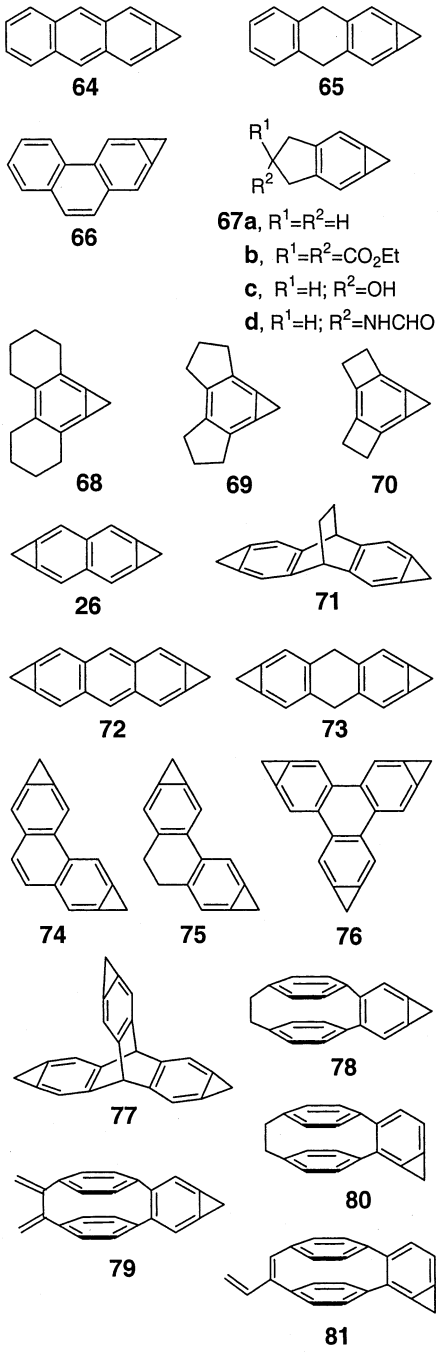
The sequence is conveniently illustrated for cyclopropa[*b*]naphthalene (**6**),[95] its 4,5-dimethyl derivative **62**[96] and the 3-aza analogue, 1*H*-cyclopropa[*g*]quinoline (**63**)[95] in Scheme 13. In these cases, the 1,3-dienes needed are orthoquinodimethanes, and it must be noted that their Diels−Alder cycloadditions to **60** do not proceed as efficiently as do those of simpler dienes. However, the subsequent bis-dehydrohalogenations give excellent yields of **6** (>95%), **62** (85%), and **63** (82%).

Scheme 13

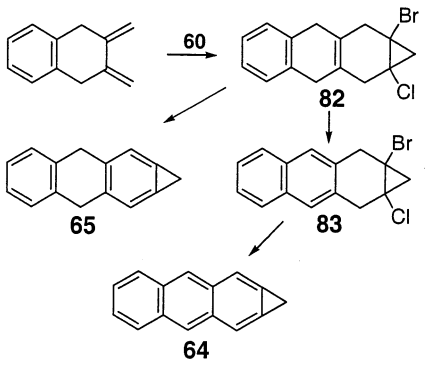


The cycloproparenes **64**−**81** displayed in Chart 1 result from Diels−Alder addition of cyclopropene **60** with the relevant diene and subsequent double dehydrohalogenation. They are formed in good-to-excellent yields and serve to illustrate the scope and utility of the reaction sequence. Many of these compounds are either not formed at all, or are available only in low yield by application of other procedures. For example, cyclopropa[*b*]anthracene (**64**) is available in 42% yield from this bis-elimination elimination sequence (Scheme 14).[97] The cycloaddition of requisite diene to **60** proceeds in 76% yield and DDQ-induced aromatization of the central ring of **82** occurs with 64% efficiency. If, instead of dehydrogenation, the bis-elimination is performed directly on **82** then quantitative dehydrohalogenation occurs and the 3,8-dihydrocyclopropanthracene **65** is formed together with 9-methylanthracene in a ca. 3:1 ratio. What must be noted here is that earlier attempts to prepare **64** via the *gem*-dichlorocyclopropene analogues of **82** and **83** gave 9-methylanthracene only (cf. Scheme 8).[62] A directly analogous series of experiments lead to cyclopropa[*b*]phenanthrene (**66**) with an 89% yield in the final step. Here again use of the *gem*-dichloro protocol gives only ring

Chart 1

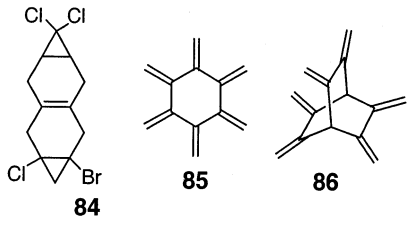


Scheme 14



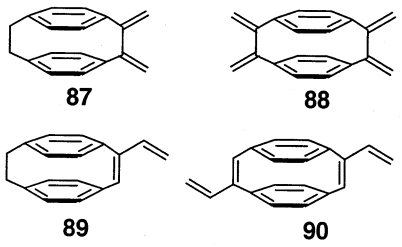
cleaved (chloromethyl)phenanthrenes.[74] It is the result of these and the studies recorded earlier that confirm the syntheses of linear cyclopropanes via the *gem*-dichloro protocol fails beyond cyclopropa[*b*]-naphthalene as products of dehydrogenative ring opening dominate.

In similar vein, the dihydrocyclopropindenes **67a**−**d** (50−75%)[86] and the tris-ring fused aromatics **68**−**70** (53, 55, and 83%, respectively)[98] are now easily available. A pathway that simultaneously involves both this and the *gem*-dichlorocyclopropane sequence has also prepared dicyclopropanaphthalene **26**, available also from the *gem*-dichlorocyclopropane protocol. Thus, treatment of the bromotrichloride **84** with potassium *tert*-butoxide in THF gives **26** in 52% yield.[99] However, this is by no means the only dicyclopropanes available. Whereas **26** was first prepared in 1974,[56] the bromochlorocyclopropane approach has made such compounds more easily available as illustrated by **71**,[100] the anthracenes **72** (18%), and **73** (31%), and the phenanthrenes **74** (84%) and **75** (77%) (Chart 1).[99] It is more than interesting to note that the yield of the dicyclopropanthracene products is markedly lower than those for the phenanthrene analogues. Once again one cannot but notice a definite avoidance of aromatization to give a cyclopropanes in the linear acene series. To date, no homologues of tetracenes or higher have been prepared by an elimination protocol that effects the final aromatization of a preformed ring system. However, the provision of such derivatives by dimerization of lower members of the series has been achieved (see section IIIA).[101]



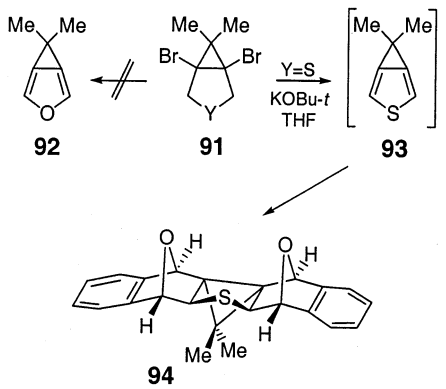
If an appropriate multiple cissoid diene is available then there appears to be almost no limit to the way in which the cyclopropanes moiety can be incorporated into organic structures. Thus, Billups[102] has show that the symmetrical tricyclopropanes **76** and **77** (Chart 1) can be obtained from hexaradialene **85** and hericene **86**, respectively, by way of 3-fold Diels−Alder cycloadditions with **60**. Not surprisingly, there is no control in the regiochemistry of addition, but this is incidental to the outcome as the product from elimination is symmetrical. Whereas the hexakisdehydrohalogenation of adduct from **85** proceeds to give **76** in 20% isolated yield under normal reaction conditions (potassium *tert*-butoxide/THF, −50°C), the analogous sequence from **86** was only effected by use of the same base with *N*,*N*-dimethylformamide and hexamethylphosphoramide at room temperature; the yield of product **77** was, however, a respectable 50%.[102]

The most recent novel hydrocarbon ring systems synthesized have come from a collaborative venture between the groups of Billups and Hopf.[103] The cyclopropacyclophanes **78**−**81** (Chart 1) were obtained from use of synthon **60** with the dienes **87**−**90**. A point to note here is that the limited stabilities of the dienes restrict the temperature at which cycloaddition to **60** can be performed to ca. −20 °C. At this temperature, the reactivity of **60** is low so that poor conversion yields are recorded and bis-additions to **88** and **90** are precluded.



A number of cyclopropanes have been approached by way of bis-dehydrobromination. The ready availability of 1,2-dibromocyclopropene at low temperatures[94] has led to its use in the preparation of 1,6-dibromobicycloheptenes as progenitors of cyclopropanes. For example, synthesis of the *gem*-dimethylbicycles **91** (Y = O or S) has been accomplished[68] and by virtue of the methyl substituents any subsequent elimination must proceed to give unsaturation in the five-membered ring. Unfortunately, dehydrobromination of the oxygen heterobicycle **91** (Y = O) does not occur upon treatment with *tert*-butoxide in THF at room temperature and cyclopropafuran **92** remains elusive. However, the same reagent in the range 0−25 °C consumes the thiabicycle **91** (Y = S). While cyclopropathiophene **93** could not be isolated (Scheme 15), its presence was shown

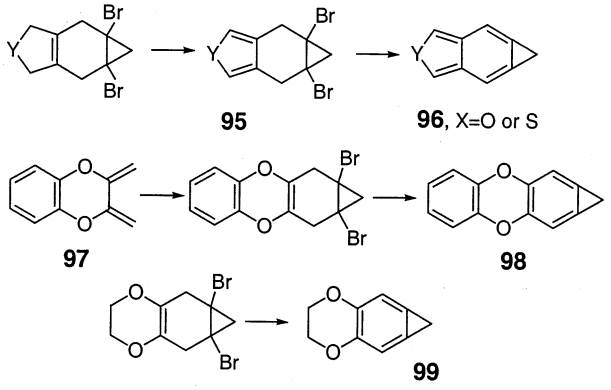
Scheme 15



from mass spectral analysis of reaction aliquots that gave the molecular ion peaks expected for **93** at *m/z* 124 (100), 125 (10), and 126 (6%). In the presence of isobenzofuran (but not furan or DPIBF), the double Diels−Alder adduct assigned as **94** is isolated. Although sequential interception of each newly formed π bond cannot be excluded, the mass spectral evidence strongly supports the formation of **93** as a reactive molecule.

Bis-dehydrobromination of **95** aromatizes the bicycle to provide the cyclopropa-isobenzofuran and -thiophene derivatives **96** (Y = O or S) (Scheme 16)[92]

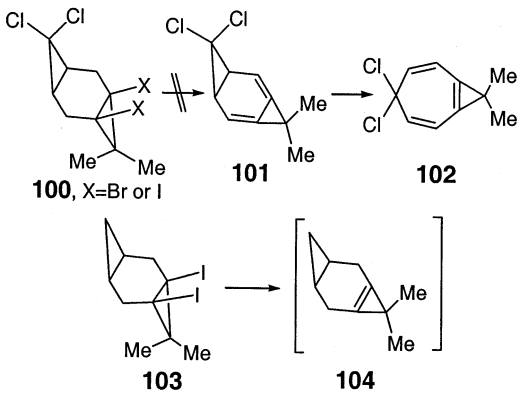
Scheme 16



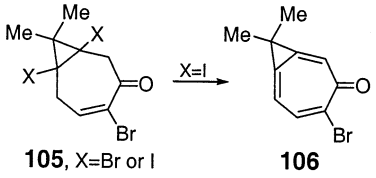
in a reaction that is directly analogous to the synthesis[86] of the *gem*-difluorobenzothiophene **59** from dichloride **58** (Scheme 11). Use of 1,2-dibromocyclopropene in trapping orthoquinodimethane **97** has provided the essential precursor to the cyclopropa-fused dibenzodioxin **98**. Compound **98** can be generated in solution, but it has quite limited lifetime because of ring opening and dimerization.[104] Precisely the same situation pertains to the stability of the simpler benzodioxin **99** as it too eludes isolation.[22]

Antiperiplanar elimination of HBr from the bridge positions in the tricyclo[5.1.0.0^{3,5}]octane series has proved futile. Although the use of *gem*-dihalo derivatives in synthesis[105] dates from the late 1970s, Simms and Wege[106] have now assembled a range of bridge halogenated derivatives with a view to preparing cyclopropacycloheptatrienes (Scheme 17). The removal of the bridge bromine atoms from **100** (X = Br) by dehydrobromination could not be effected under a variety of reaction conditions. The authors state that if the X-ray crystallographic structure of

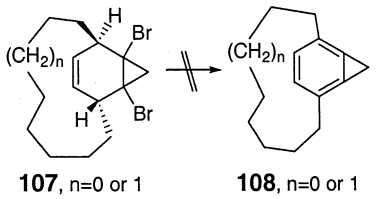
Scheme 17



dibromodichloride **100** is maintained in solution then the relevant dihedral angle for elimination is a mere 110°; antiperiplanar elimination is thwarted and **101** is unlikely to form. Additionally, the prospect of a *syn*-elimination is strongly disfavored on energetic grounds. Even the di-iodide analogue (**100**, X = I) displays remarkable thermal stability and no products of elimination were detected. This leaves **102** and its derivatives as targets for alternative syntheses. The availability[106] of di-iodide **103** did not assist as attempted bis-dehydroiodination instead led to deiodination with products resulting from trapping the bridge double bond of cyclopropene **104**. The same workers prepared the bromotropone progenitors **105** (X = Br or I) and upon treatment with triethylamine in dichloromethane the di-iodide gave cyclopropatropone **106** in 81% yield; the dibromide did not behave analogously but gave a rearrangement product instead.

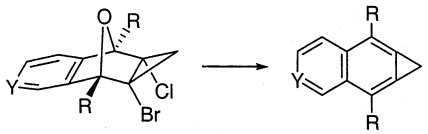


We have seen that the cyclopropparene moiety has been incorporated into the [2.2]cyclophane framework through the derivatives **78**−**81**. Garratt, Payne, and Tsotinis have attempted to build cyclopropapara-cyclophanes by using the dehydrobromination strategy.[107,108] To this end, the "in-out" bicycloalkenes **107** (n = 0 or 1) were prepared from conventional Diels−Alder additions of the requisite *E,Z*-diene with dibromocyclopropene. However, subsequent dehydrobrominations using *tert*-BuOK in either THF or DMSO gave only intractable materials. It would be interesting to see the effects of *N,N*-dimethylformamide and hexamethylphosphoramide (as used by Billups[102] for **77**) on these bicycles.



While dehydrohalogenation has provided the predominant mode of aromatizing the 1-bromo-6-chlorobicycloheptenes, it is not the only method that has been employed. The deoxygenation of furan adducts of butadienes by low valent titanium provides a convenient and useful synthesis of novel aromatics,[109] and because this same reagent reduces vicinal dihalides to alkenes, extension to cyclopropparene synthesis has been addressed.[110,111] Thus, adducts of bromochlorocyclopropene **60** with various furans are aromatized from 2-fold metalation at the bridge sites and removal of the oxygen bridge by β-elimination. The reagent may be prepared from $TiCl_3$ and any one of $LiAlH_4$, BuLi, or MeLi. The adducts **109**−**111** are efficiently aromatized with greater or lesser amounts of naphthalene side products depending upon the

origin of the titanium reagent.[111] Use of 4-aza-2,7-dimethylisobenzofuran with **60** gives the analogous bromochloro adduct **112**, which is likewise aromatized to give the cyclopropisoquinoline derivative **115**, the homologue of **63**.[112]

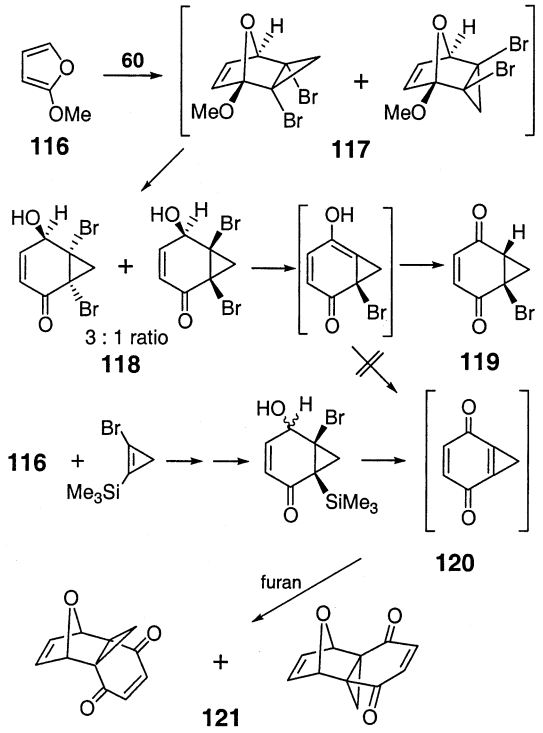


109, Y=CH; R=H
110, Y=CH; R=Me
111, Y=CH: R=Ph
112, Y=N, R=Me

6, Y=CH; R=H
113, Y=CH; R=Me
114, Y=CH: R=Ph
115, Y=N, R=Me

Reaction of 2-methoxyfuran (**116**) with **60** gives a mixture of enones **118** in a 3:1 ratio presumably via the oxatricyclooctanes **117** that do not survive the workup conditions (Scheme 18).[69] Brief treatment of

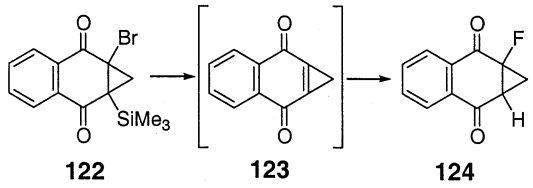
Scheme 18



the **118** mixture with DBU affords the bicyclic enedione **119** from dehydrobromination of the enol intermediate, and not the desired cyclopropaquinone **120**. This has parallel in the early work of Ullman and Buncell[12] as discussed in the early reviews.[11,15] Quinone **120** has been prepared,[113] however, as discussed below and in section IIB, 4(b).

3. By Employing 1-Bromo-6-trimethylsilyl Derivatives

Despite the inability to transform **118** into cyclopropaquinone **120** (Scheme 18), a change in the cyclopropene substituents to force the elimination across the bridge has provided this compound as a very reactive molecule from a series of directly analogous experiments.[69] Commencing with 1-bromo-2-trimethylsilylcyclopropene rather than dibromocyclopropene, addition to **116** provides for subsequent fluoride ion-induced desilylation to generate the necessary double bond in the three-membered ring; **120** is formed and was trapped as *endo* and *exo* Diels−Alder adducts **121** in a 9:2 ratio (Scheme 18).[69] The homologous naphthoquinone **123**, synthesized in the same way, is somewhat more stable and is intercepted by fluoride ion at −78 °C as **124** (24%). Furan trapping of **123** gives analogues of **121** with the *endo*-product again dominating (2:1).[69]

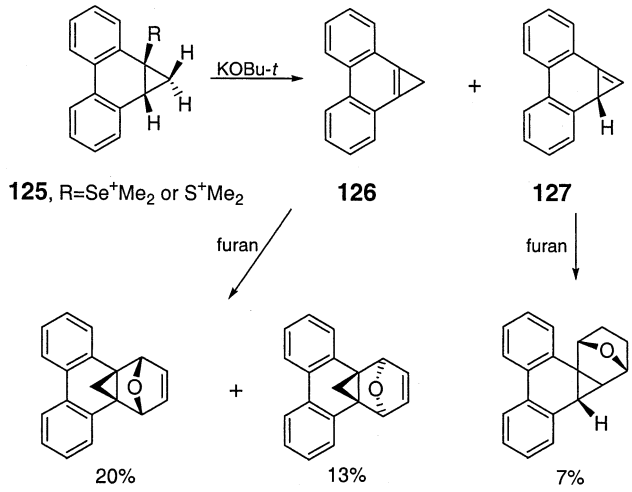


122 **123** **124**

4. By Employing Other Bicyclo[4.1.0]heptenes

(a) With Dehydrohalogenation. An obvious advantage of 1,2-elimation across the bridge sites is the ability to target[114−117] the synthesis of 1*H*-cyclopropa[*l*]phenanthrene (**126**) more effectively than by routes involving C-1 substituents.[6,118] Here, the successful studies employed thermal *syn*-eliminations across the bridge bond as depicted by Scheme 19. Thus, the

Scheme 19



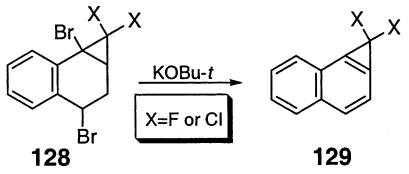
125, R=Se^+Me_2 or S^+Me_2 **126** **127**

20% 13% 7%

reactive parent hydrocarbon **126** is formed upon treatment of the selenonium[114,115] or sulfonium[117] salts **125** with *tert*-BuOK. It is trapped by furan as *endo* and *exo* Diels−Alder adducts (33%, 3:2). The removal of the *syn*-bridge hydrogen atom occurs in competition with that from C-1. However, the desired bridge olefin, cycloproparene **126**, appears to dominate since the trapping gives products from capture of it and the Δ^1-alkene **127** in a ca. 5:1 ratio (40% in total). This appears to be too high to account either for a rate difference and/or steric constraints that favor **126** in the cycloaddition.

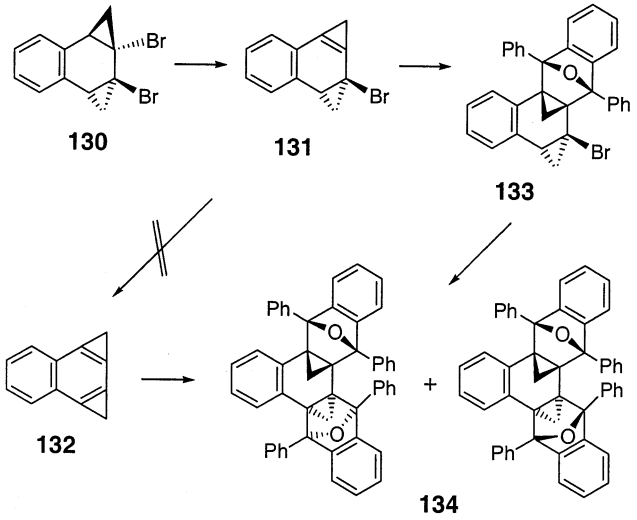
The synthesis of the angular cyclopropa[*a*]naphthalene **129** has posed problems for synthesis because only a *syn*-elimination protocol can be applied easily. While desilylation procedures have not been applied—the requisite diene for bromosilylcyclopropene addition would encompasses a benzenoid π bond, viz., styrene—bis-dehydrobromination of **128** is effective.

Müller and Nguyen-Thi[89,91] have shown that the dibromides **128** (X = F or Cl) are easily prepared from 1,2-dihydronaphthalene and that upon treatment with *tert*-butoxide the 1,1-dihalocyclopropa[*a*]naphthalenes **129** (X = F or Cl) are formed as somewhat unstable compounds.



One of the recorded attempts to produce a dicyclopropabenzene has much in common with Müller's synthesis of **129**. Thus, Brinker and co-workers synthesized the benzotricyclooctane **130** from *o*-divinylbenzene and subjected it to classical dehydrobromination procedures (Scheme 20).[119] From a very

Scheme 20



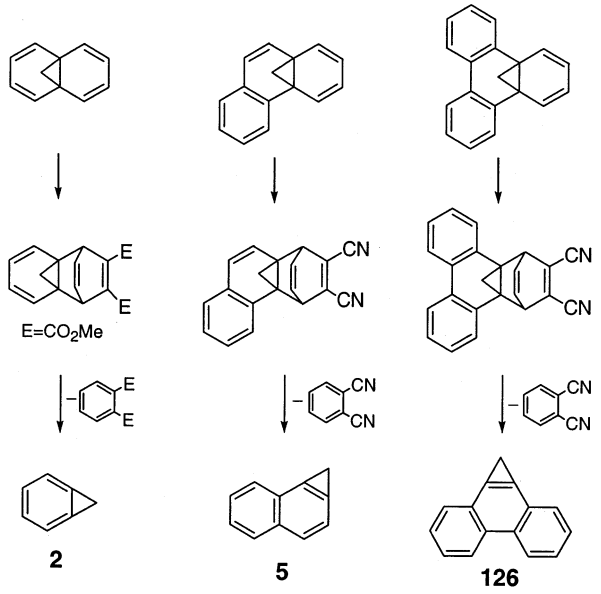
careful study, they were able to show that elimination gives **131** that is trapped by added DPIBF as **133**. Isolation of this and resubjection of it to the elimination conditions gives a new ring-fused cyclopropene that is captured by the diene as the syn and anti adducts **134**. The isomer ratio was the *same* as that recorded when **130** reacts directly with excess base and excess added diene to give the same compounds in a one-pot procedure. Thus, **131** is captured by DPIBF more rapidly that can form the desired dicyclopropa[*a*,*c*]naphthalene **132**, and it seems unlikely that this is involved at all.

Other approaches to the cyclopropabenzenes involving the removal of bridge substituents include attempted decarboxylation of bridge acids that were unsuccessful and justify no further discussion here.[15,120,121]

(b) With Flash Vacuum Pyrolysis. The fragmentation of an appropriate disubstituted bicyclohepta-2,4-diene to give a cyclopropabenzene as one of the two components from Alder-Rickert cleavage provided cyclopropabenzene (**2**) for the first time.[2] The use of flash vacuum pyrolysis (FVP) methods have served the cyclopropabenzene field rather well since the retrodiene reaction invariably gives the desired product and it tends to proceed with modest efficiency. The disadvantage is that the substrates needed are frequently not the easiest to prepare.

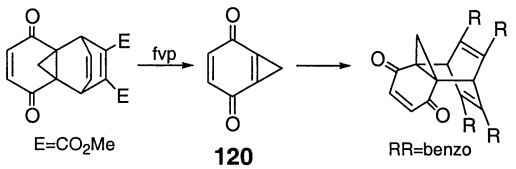
The synthesis of **2** commenced with 1,6-methano-[10]annulene which adds dimethyl acetylenedicarboxylate (DMAD) via its ring closed bis-norcaradiene valence isomer as shown in Scheme 21.[2] The product,

Scheme 21



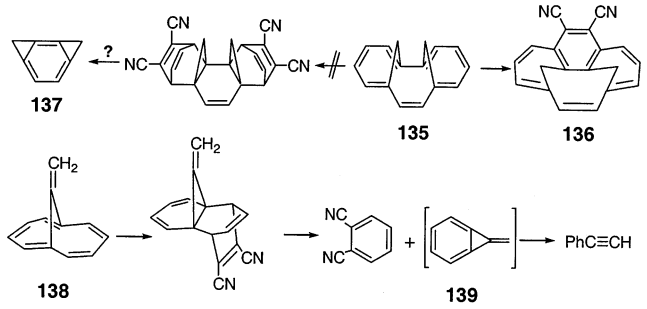
a new norcaradiene, is the synthon for **2**. Construction of other carbocycles has allowed for comparable alkyne additions (usually with dicyanoacetylene (DCA) but sometimes also with DMAD), and application of FVP techniques has provided cyclopropa[*a*]naphthalene (**5**) (unavailable by other routes),[122] and cyclopropa[*l*]phenanthrene (**126**).[114] The order of stability of the compounds is **2** > **5** > **126**; it decreases as the π character of the bridge bond increases. Whereas **2** is an odoriferous liquid stable for many months as a solution in pentane in the refrigerator, **5** decomposes upon melting at 20 °C, and **126** is stable only for a few days at −78 °C in the solid state.

Cyclopropabenzoquinone (**120**) has been discussed earlier (see Scheme 18). However, the first report of this reactive molecule came from FVP studies. Oda and co-workers showed and that the highly reactive cyclopropene could be generated and trapped by cycloaddition across the 9,10-positions of anthracene as shown.[113] However, the later procedures of Wege[69] are more appropriate for any study of the compound.



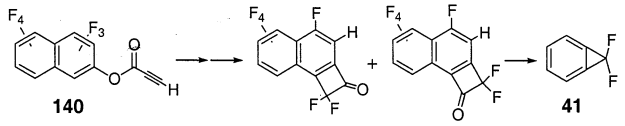
The *syn*-bismethano[14]annulene **135**, prepared in 1986 by the Vogel group,[123] has all of the necessary features for bis-addition of an alkynyl dienophile that would provide the essential progenitor for **137**. However, while the authors found that addition of DCA does take place, it is only to the bay region

"diene" to give **136**, and not across the bridge centers as is required for the ultimate preparation of **137**. It is not surprising that the existence of 11-methylidene-1,6-methano[10]annulene (**138**)[124] has prompted dienophile addition. It proceeds by analogy to the parent annulene and subjection of the DCA adduct to FVP conditions results in *o*-dicyanobenzene and phenylacetylene. Methylidenecyclopropabenzene (**139**) is not isolated, but it seems likely that it is the primary reaction product, which rearranges under the conditions. Matrix studies and low-temperature interception of the primary product are needed.



The pyrolysis of the heptafluoropropynoate **140** has been reported to take an unusual course that involves initial intramolecular Diels−Alder reaction between the triple bond and its attached trifluoro-substituted benzenoid ring.[125] A subsequent complex pathway has been proposed to account for the formation of cyclobutenones as the major products (Scheme 22);

Scheme 22



gem-difluorocyclopropabenzene (**41**) also is present and arises by ring contraction of the four-membered ring upon decarbonylation, cf. path *f*, Scheme 1. Cyclopropabenzene (**2**) is likewise formed by decarbonylation of benzocyclobutenone on FVP, and care must be exercised when using this technique as a preparative route to the four-membered ketone.[126] The formation of oxocyclopropabenzenes (benzocyclopropenones) by ring contraction under FVP conditions is also well documented but discussion is deferred to section IID.

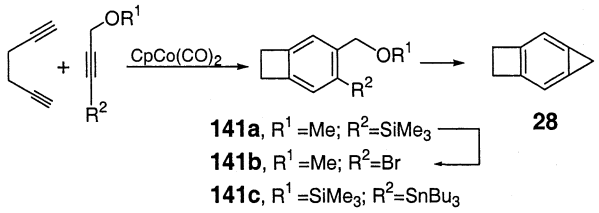
C. From *o*-Substituted Benzyl Derivatives by 1,3-Elimination

As seen in the foregoing discussion, the availability of cycloproparenes from preformed ring systems offers a wide range of possibilities. Nonetheless, use of an aromatic substrate carrying appropriate *o*-substituents should not be overlooked as the recent developments in organometallic chemistry, coupled with the leaving group abilities, offers much for the future.

Some of the earliest recorded approaches to parent **2** and its arene homologues **6** and **126** include uses of *o*-bromobenzyl bromides[127] and the corresponding methyl ethers.[128,129] The ring-closing elimination sequence (path *e*, Scheme 1), which provides cyclobutabenzenes in almost quantitative yields,[130] has had little success in the cycloproparene series[15,127−129] until recently.[131]

In 1975, Saward and Vollhardt[132] reported a synthesis of rocketene **28** involving the 1,3-elimination sequence. Thus, metalation (BuLi) and elimination (Scheme 23) followed transformation of the silyl ether

Scheme 23



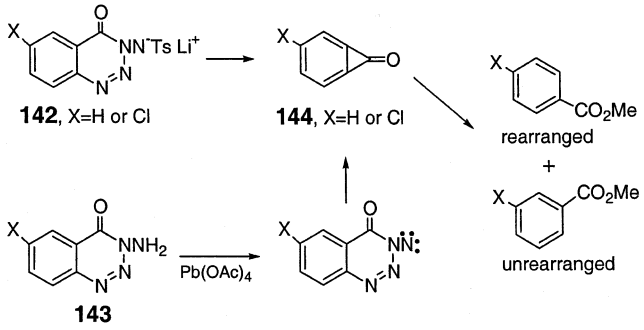
141a into the *o*-bromoether **141b**. However, the yield of **28** from the cyclization was a mere 5% and no match for the ca. 40% obtained in the *gem*-dihalocyclopropane route (section IIB.1). By changing the leaving groups on **141** to the silyl ether (R^1) and tributylstannyl (R^2) of **141c**, McNicholls and Stang[131] were able to effect the ring closure in 65% yield, thus making **28** readily available. The reaction sequence provides **141c** from 1,5-diyne and yne by analogy to the Vollhardt synthesis, but it must be noted carefully that the experimental details provided by the authors omit the critical requirement of irradiation (from a projector bulb close to the reaction vessel) in order to obtain **141c**.[133] This success in providing the highly strained **28** argues forcefully for comparable *o*,α-eliminations to provide other cycloproparene derivatives.

D. Oxocyclopropareneś (Benzocyclopropenones)

The transient existence of cycloproparenones, e.g., **144** (oxocyclopropabenzene or benzocyclopropenone), dates almost to the time of the first cycloproparene synthesis. In studies on the thermal decomposition of phthalic anhydride[134,135] and indanetrione[136] losses of carbon dioxide and carbon monoxide, respectively, provide the open form of **144** en route to benzyne. Shortly thereafter, the existence of **144** in solution was established by the groups of Rees[137,138] and Burgess,[139] but the compound is so sensitive to electrophiles and nucleophiles that it is not capable of isolation and characterization under normal conditions. Although it had been isolated in low-temperature matrixes[140,141] and in solution at 193 K,[142] it has now been incarcerated inside a molecular container such that it can held at ambient temperatures.[143,144]

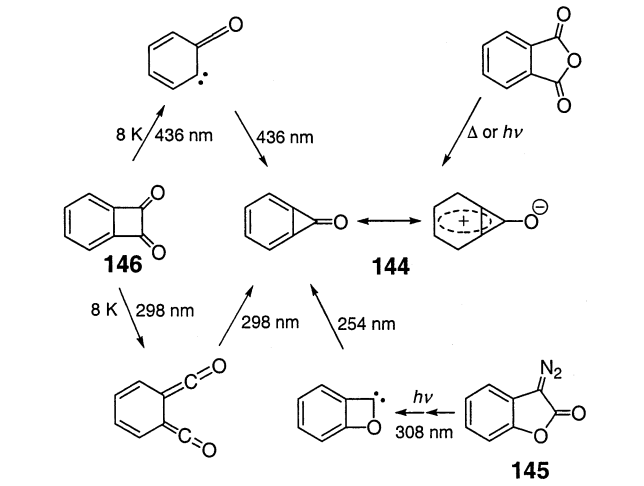
Photolysis of **142** in methanol,[139] and upon lead(IV) acetate oxidation[137,138] of **143** benzoate esters are formed (Scheme 24). The aminotriazinones **143** give rearranged and unrearranged esters, whereas *m*-chloro-**142** gives only rearranged methyl *p*-chlorobenzoate. These studies demand a symmetrical intermediate and ketone **144** is the clear choice. The observation of 7−13% of rearrangement in the pathway from the triazinones provides a minimum estimate of proportion of reaction that proceeds through ketone **144**.

Scheme 24



The photodecomposition of phthalic anhydride has continued to receive attention, and it has now been shown that **144** is a minor but definite product from irradiation at 308 nm;[145] *o*-benzyne is the major product formed from decarbonylation and decarboxylation of this and fluorinated derivatives.[145] The diazobenzofuranone[146] **145** also serves as a progenitor to **144**, but it is the photodecarbonylation of cyclobutabenzedione **146** that has received the most attention (Scheme 25). Originally examined by Chapman and

Scheme 25



co-workers,[147] the reaction has provided **144** in a low-temperature matrix from which IR and UV spectra have been recorded[140,141] and, after transfer into solution, ^{1}H and ^{13}C NMR spectra (see section V).[142]

The most notable development in oxocyclopropabenzene chemistry has been the photodecarbonylation of **146** in a hemicarcerand.[143,144] Use of a calix[4]arene molecular container (Figure 1) allows for incarceration of benzocyclobutenedione and upon irradiation at wavelengths greater than 400 nm carbon monoxide is ejected. Whereas **144** has only been examined previously in solution at temperatures

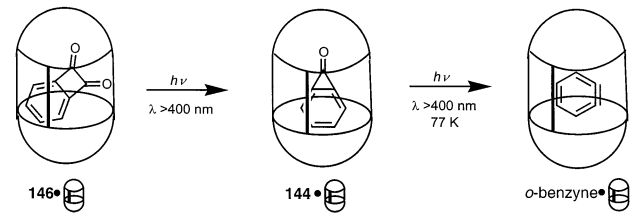
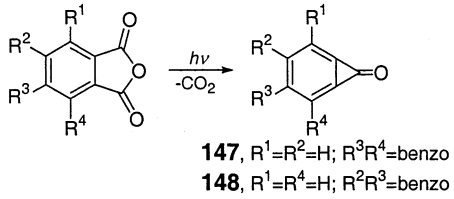


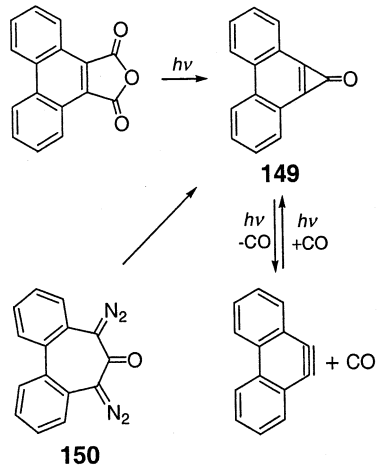
Figure 1. Oxocyclopropabenzene (**144**) formed inside a host.

below −60 °C,[142] generated in this way the surrounding host shell protects it from hydrolysis and it is stable to ambient temperatures; slow decomposition to benzoic acid occurs over a period of days using water-saturated chloroform.[143] Not only have spectroscopic data have been recorded but also the X-ray crystal structure has been measured at ambient temperature although the data have yet to appear.[144] Upon photolysis in the range 270−290 nm **144** loses carbon monoxide and incarcerated *o*-benzyne is produced; its spectroscopic data have been recorded also.[144]

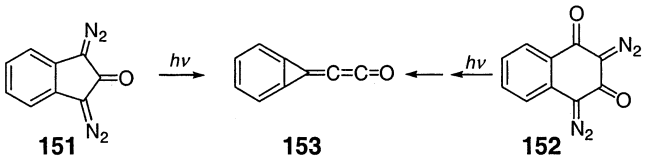


The existence of oxocyclopropabenzenes is not restricted simply to the benzene derivative. Photolysis of naphthalene-1,2-dicarboxylic anhydride at 355 nm in an argon matrix at 11 K leads to the ejection of carbon dioxide and formation of **147** as monitored by IR spectroscopy. No bands due to CO were recorded but subsequent photolysis ejected CO with concomitant formation of 1,2-didehydronaphthalene.[148] Not surprisingly, similar treatment of the isomeric naphthalene-2,3-anhydride gives oxocyclopropa[*b*]naphthalene **148**.[149] Again, photolysis of the phenanthrene anhydride provides oxocyclopropa[*l*]phenanthrene **149** in an argon matrix at 10 K and use of the bisdiazoketone **150** has also been found effective.[150] Moreover, subsequent photodecarbonylation to phenanthryne is *reversible* in the matrix upon photoexcitation (Scheme 26).

Scheme 26

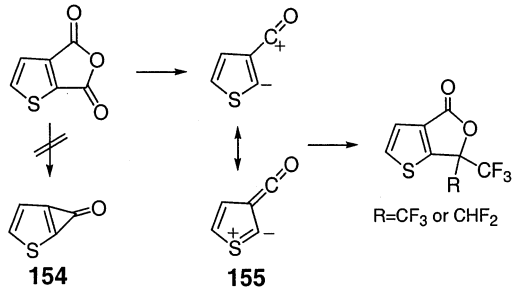


The group of Tomioka at Mie has also addressed the five- and six-membered bisdiazoketones, **151** and **152**. They have found that both provide a ketone that is tentatively assigned as **153**, the only reported cumulenone in the cycloproparene series.[151−153] The existence of the transient cyclopropenone-fused heterocycle **154** was proposed by Reinecke[154] from trapping experiments with hexa- and penta-fluoroacetone in 1980 (Scheme 27). Much more recently, the

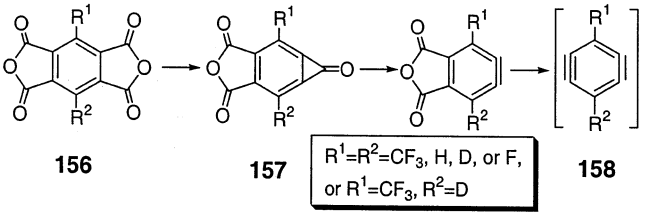


involvement of this ketone has been negated from use of matrix studies. Thus, Teles, Hess, and Schaad[155] have shown that the pseudocarbene ring opened form **155** of **154** is formed directly and that it is this species that is trapped. Ab initio calculations place **154** and **155** very close in energy, but it is the later that is more stable.

Scheme 27



Finally, the past six years have seen major developments in didehydrobenzene chemistry to the extent that two bis-benzyne have been characterized by IR spectroscopy of the matrix-isolated material.[156−158] Irradiation of the dianhydride **156** ($R^1 = R^2 = CF_3$) induces loss of CO_2 with formation of benzocyclopropenone **157** ($R^1 = R^2 = CF_3$).[156] Further irradiation causes CO_2 and CO loss with formation of the bis-benzyne **158** ($R^1 = R^2 = CF_3$); in no experiment was an oxocyclopropabenzyne detected. The study now includes **156** ($R^1 = R^2 = CF_3$, H, D, or F, and $R^1 = CF_3$, $R^2 = H$), but the photolyses did not provide the critical evidence needed to characterize any tetradehydrobenzene other than difluoro **158** ($R^1 = R^2 = F$).[157,158]

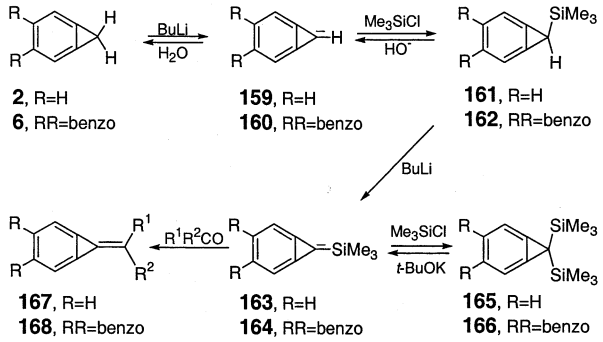


E. Alkylidenecycloproparenes

The existence of stable, colored crystalline alkylidenecycloproparenes dates to 1984 and the class of compounds has been discussed independently in review form previously[16,17] as well as within a chapter on the cycloproparenes.[4] The historical aspects of this class of compounds are not presented again, but it is noteworthy that the members now number well in excess of 100. The properties have provided for much fascination especially because of the incorporation within the one molecule of a triafulvene, a [3]-radialene and the cycloproparene.

The original synthesis[159,160] still provides the most useful route to these compounds and commences with a cycloproparene hydrocarbon, e.g., **2**, that is subjected to reaction with BuLi whereupon a benzylic methylene proton is removed and a cyclopropareny anion, e.g., **159**, is formed (Scheme 28). Displacement

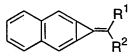
Scheme 28

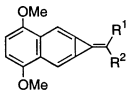


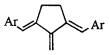
of chloride ion from chlorotrimethylsilane by the anion provides a silane, e.g., **161**. In turn, this is deprotonated to generate the even more stable α-silyl anion, e.g., **163**, which is able to react with an aldehyde or ketone to give the desired exocyclic alkene, e.g., **167**, in a silyl-Wittig or Peterson olefination (Scheme 28). As a synthesis of alkylidenecyclopropareneS, the protocol is without precedent.[17] In the cyclopropabenzene series, the reaction sequence can be employed as a one-pot procedure with sequential additions of base, chlorotrimethylsilane, base, and carbonyl compound.[160] However, for the cyclopropanaphthalene series mono-silane **162** is not easily accessible and has been isolated only by desilylation of the disilane **166**, and then only with difficulty.[161] Treatment of **6** sequentially with stoichiometric quantities of BuLi and Me_3SiCl does not lead to **162** but gives almost equal quantities of regenerated **6** and disilane **166** in near quantitative yield. Anion **164** is undoubtedly more stable than its nonsilylated counterpart **160** and is formed from deprotonation of **162** by unreacted anion **160**, thus providing **6** and **164**. Independent studies have shown that upon reaction with catalytic amounts of hydroxide ion and water disilane **166** is sequentially desilylated and transformed to hydrocarbon **6** almost quantitatively.[162] Generated in this way under anhydrous conditions, anion **164** can be intercepted by other electrophiles.[161−163]

The transformation of **6** into **166** in good yield is effective with an excess of the above reagents thereby providing the ideal synthon for subsequent preparation of **168**. While the original experimental procedures have been improved upon, they have not necessarily been optimized.[164] The protocol of Scheme 28 works well for arylaldehydes and diaryl ketones, but the presence of an α hydrogen atom allows for competing enolate ion formation and this invariably leads to reduced product yields or, in many cases, none of the desired product at all. The route suffers from its failure to yield the parent exocyclic alkenes **167/168** ($R^1 = R^2 = H$) either as isolable compounds or as detectable reactive molecules in solution. The range of exocyclic olefins available in the cyclopropa[*b*]naphthalene series by this protocol is given in Table 1 and the much more limited range of benzenes

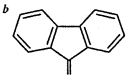
Table 1. Alkylidenecyclopropa[*b*]naphthalenes 168 from Disilane 166

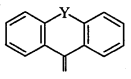


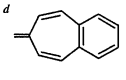


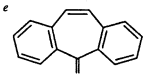
Entry	R^1	R^2	Yield %	mp (°C)	μ (D)	Ref.	Entry	R^1	R^2	Yield %	mp (°C)	μ (D)	Ref.
1	H	*t*-Bu	68	59-60		160							
2	H	Ph	59	114-7	1.3	160							
3	H	4-MeC_6H_4	63	143-5	1.1	165	75	H	4-MeC_6H_4	35	147-8	0.6	165
4	H	4-$Me_2NC_6H_4$	94	141-2	1.8	164	76	H	4-$Me_2NC_6H_4$	63	164-5	1.4	64,165
5	H	3-$MeOC_6H_4$	74	150-1	1.1	165	77	H	3-$MeOC_6H_4$	35	122-4	1.5	165
6	H	4-$MeOC_6H_4$	52	115-8	1.4	160,168	78	H	4-$MeOC_6H_4$	83	149-50	0.9	165
7	H	4-$MeSC_6H_4$	61	137-8	1.3	169	79	H	4-$MeSC_6H_4$	25	156-7	0.8	165
8	H	4-FC_6H_4	71	187-9	1.3	165	80	H	4-FC_6H_4	62	122-3	1.6	165
9	H	2-ClC_6H_4	73	147-8		170							
10	H	4-ClC_6H_4	48	154-6	1.4	165,168	81	H	4-ClC_6H_4	78	116-8	1.7	165
11	H	4-BrC_6H_4	55	146-8	1.4	165	82	H	4-BrC_6H_4	33	118-20	1.8	165
12	H	2,4-$(MeO)_2C_6H_3$	45	122-3		169	83	H	2,4-$(MeO)_2C_6H_3$	61	167-8		64
13	H	2,4,6-$(MeO)_3C_6H_2$	63	114-5		169							
14	H	4-$O_2NC_6H_4$	8	193-4	[a]	165,171	84	H	4-$O_2NC_6H_4$	12	147-9	[a]	165
15	H	4-NCC_6H_4	17	187-91	2.5	165,172	85	H	4-NCC_6H_4	22	136-8	2.9	165
16	H	4-$CF_3C_6H_4$	62	163-4	3.0	165							
17	H	1-naphthyl	30	228-30		173							
18	H	2-naphthyl	43	228-30		173							
19	H	9-anthryl	45	191-2	[a]	173							
20	H	2-pyridyl	50	129-31		164,165							
21	H	4-pyridyl	39	183-4	3.4	164,173							
22	H	2-(1-Methylpyrrolyl)	87	180-2		164,165							
23	H	2-furyl	42	135-6	3.0(5)	164,165							
24	H	2-thienyl	34	188-90	2.8	164,165	86	H	2-furyl	52	146-8	2.6	165
25	H	ferrocenyl	66	159-60	3.4	164,165	87	H	Ferrocenyl	50	170-1	2.9	165
26	CF_3	CF_3	25	oil		174							
27	*t*-Bu	*t*-Bu	17	68-9		174							
28	*t*-Bu-C≡C	*t*-Bu-C≡C	73	93-4		174							
29	Ph-C≡C	Ph-C≡C	49	102-4		174							
30	Ph	Me	39	94-5		160							
31	Ph	$Me(CH_2)_3$	57	66-8		175							
32	Ph	CF_3	10	solid		160							
33	Ph	Ph	95	110-11	0.4	160,168	88	Ph	Ph	57	188-9	1.2	64,165
34	Ph	PhCO	35	83-4		174							
35	Ph	(*E,E*)-PhCH=CH-CH=CH	50	182-3	1.4	165	89	Ph	(*E,E*)-PhCH=CH-CH=CH	23	136-8	1.9	165
36	Ph	4-$Me_2NC_6H_4$	20	167-9	1.5	165	90	Ph	4-$Me_2NC_6H_4$	56	173-4	1.1	165
37	Ph	4-$MeOC_6H_4$	65	118-9	1.2	165	91	Ph	4-$MeOC_6H_4$	74	131-3	0.8	165
38	Ph	4-$C_6HS(4'-C_6H_4Me)$	63	oil		164							
39	Ph	4-FC_6H_4	51	105-6	0.9	165,176	92	Ph	4-FC_6H_4	45	169-71	1.2	165
40	Ph	3-Cl-C_6H_4	55	163-5	1.6	165	93	Ph	3-Cl-C_6H_4	75	155-7	1.9	165
41	Ph	4-ClC_6H_4	44	161-3	1.1(5)	165	94	Ph	4-ClC_6H_4	50	133-5	1.2(5)	165
42	Ph	4-BrC_6H_4	90	100-1	1.2	165,175	95	Ph	4-BrC_6H_4	74	181-3	1.3	165
43	Ph	4-$O_2NC_6H_4$	18	176-8	3.1	165	96	Ph	4-$O_2NC_6H_4$	19	142-4	3.5	165
44	Ph	3-$F_3CC_6H_4$	66	178-9	2.7	165	97	Ph	3-$F_3CC_6H_4$	55	155-6	3.1	165
45	Ph	4-$F_3CC_6H_4$	65	146-7	2.9	165	98	Ph	4-$F_3CC_6H_4$	81	137-8	3.2	165
46	Ph	2-thienyl	52	55-7		164							
47	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	55	179-80	3.0	164,177	99	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	21	183-5	2.3	165
48	4-$Et_2NC_6H_4$	4-$Et_2NC_6H_4$	21	188-90	2.9	165	100	4-$Et_2NC_6H_4$	4-$Et_2NC_6H_4$	10	159-60	2.3	165
49	4-$MeOC_6H_4$	4-$MeOC_6H_4$	64	134-6	2.4	168	101	4-$MeOC_6H_4$	4-$MeOC_6H_4$	16	157-8	1.7	64,165
50	4-FC_6H_4	4-FC_6H_4	32	133-5	0.9	165	102	4-FC_6H_4	4-FC_6H_4	50	168-70	1.1	165
51	4-ClC_6H_4	4-ClC_6H_4	55	146-8	1.5	165	103	4-ClC_6H_4	4-ClC_6H_4	62	137-9	1.8	165
52	4-BrC_6H_4	4-BrC_6H_4	94	193-4	1.5	165,175	104	4-BrC_6H_4	4-BrC_6H_4	72	153-5	1.8	165
53	4-$O_2NC_6H_4$	4-$O_2NC_6H_4$	84	228-9	4.3	165,171	105	4-$O_2NC_6H_4$	4-$O_2NC_6H_4$	25	177-8	4.7	165
54	3-$F_3CC_6H_4$	3-$F_3CC_6H_4$	73	109-10	3.3	165,178	106	3-$F_3CC_6H_4$	3-$F_3CC_6H_4$	83	185-7	3.9	165
55	2-thienyl	2-thienyl	59	94-5	9.1	164,173							
56	9-fluorenylidene[b]		92	259-60	3.3	168,171,179	107	9-fluorenylidene[b]		71	280sub.	3.7	64,165
57	9-(10,10-dimethyl)anthrylidene[c]		63	153-5	1.7	173,180							
58	9-(*N*-methyl)acridinylidene[c]		22	177-8	1.7	180							
59	9-xanthylidene[c]		59	219-21		173,180							
60	9-thioxanthylidene[c]		46	171-3	1.8	165,180	108	9-thioxanthylidene[c]		16	133-4	*a*	165
61	anthronylidene[c]		35	248-50		180							
62	benzo[*c*]cycloheptatrienylidene[d]		51	232dec.	1.4(5)	165,168,179	109	benzo[*c*]cycloheptatrienylidene[d]		9	177-9	1.6	165
63	dibenzo[*a,e*]cycloheptatrienylidene[e]		87	190-1	1.6	165,168,179	110	dibenzo[*a,e*]cycloheptatrienylidene[e]		35	271-2	1.9	165
64	stellylidene[f]		60	122		181	111	stellylidene[f]		42	122		181
65	6-stellonylidene[f]		62	105		181							
66	(*E*)-PhCH=CH	(*E*)-PhCH=CH	32	107-08	1.1	165							
67	(*E*)-4-MeC_6H_4CH=CH	(*E*)-4-MeC_6H_4CH=CH	55	123-4	1.6	165							
68	(*E*)-4-$Me_2NC_6H_4CH$=CH	(*E*)-4-$Me_2NC_6H_4CH$=CH	82	129-30	3.2	165							
69	(*E*)-4-$MeOC_6H_4CH$=CH	(*E*)-4-$MeOC_6H_4CH$=CH	41	165-6	2.7	165							
70	(*E*)-4-FC_6H_4CH=CH	(*E*)-4-FC_6H_4CH=CH	68	148-51	1.4	165							
71	(*E*)-4-ClC_6H_4CH=CH	(*E*)-4-ClC_6H_4CH=CH	34	138-40	1.9	165							
72		Ar = 4-MeC_6H_4	18	133-5	1.7	165							
73		Ar = 4-$Me_2NC_6H_4$	42	137-8	3.5	165							
74		Ar = 4-$MeOC_6H_4$	26	157-9	2.9	165							

[a] Insufficiently soluble

[b] 

[c] 
Y = CMe_2, NMe, O,S or CO

[d] 

[e] 

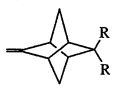
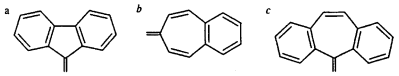
[f] 
R = H or RR = O

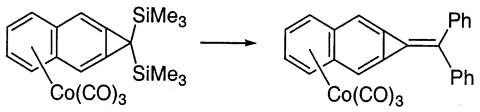
Table 2. Alkylidenecyclopropabenzenes 167 from Cyclopropabenzene (2)

Entry	R^1	R^2	Yield %	mp (°C)	μ (D)	Ref.
1	H	Ph	13	solid		160
2	H	4-$MeOC_6H_4$	31	solid		160
3	Ph	Me	10	oil		160
4	Ph	Ph	38	89-91	1.0	168
5	4-$MeOC_6H_4$	4-$MeOC_6H_4$	34	118-9	1.9	182,183
6	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	24	155-7	2.2	168,184
7	9-fluorenylidene[a]		38	180-1	2.6	168,184
8	benzo[c]cycloheptatrienylidene[b]		9	128-9		168,184
9	dibenzo[a,e]cycloheptatrienylidene[c]		11	158-9	1.2	168,184



in Table 2. Here it must be noted that the lower yields recorded for the last group of compounds reflects the four-step, one-pot procedure from hydrocarbon **2** in comparison to the two-step transformation to naphthalenes from disilane **166**. The paucity of examples in the benzene series derives not so much from difficulty in the reaction as from the severe malodor of substrate **2**! Finally, it should be noted that the range of 3,6-dimethoxy-substituted alkene derivatives, prepared from 3,6-dimethoxycyclopropa[*b*]naphthalene,[64,65,165] now greatly exceeds the published number of five.

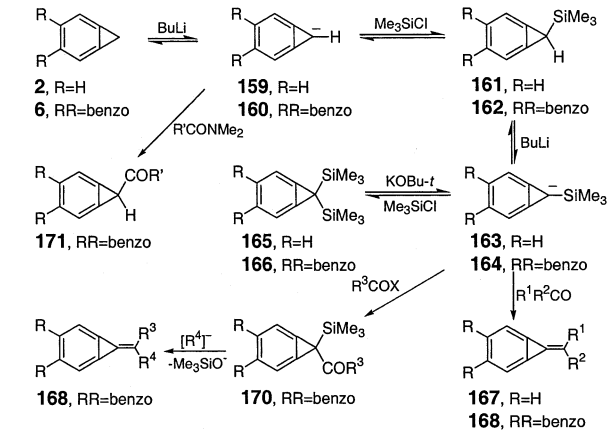
In addition to the compounds depicted in Tables 1 and 2, Müller and co-workers have used the procedures of Scheme 28 to prepare the chromium tricarbonyl derivative **169** from its disilane complex thereby demonstrating the stability of chromium-complexed cyclopropabenes to the strongly basic conditions involved.[166,167]



169

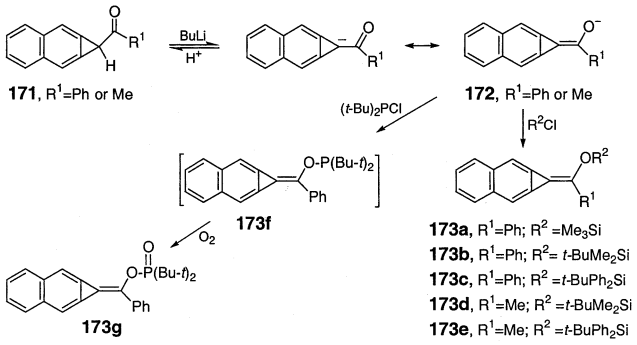
Four other routes to alkylidenecyclopropabenes have been published,[124,185−187] and a fifth that employs reversed reactivity concepts is summarized here for the first time.[188] Each of these has clear limitations and none is widely applicable. Thus, the procedures of Scheme 28 have been employed to divert anion **164** into a series of 1-carbonyl, ester, and amide derivatives **170**.[186] These subsequently react with nucleophile $(R^4)^-$ at the carbonyl center to give oxyanion, which induces loss of the silyl function and exocyclic olefin formation (Scheme 29). Whereas interception of anion **164** is reproducible with some electrophiles,[161−163,187] the isolation of alkylidene derivatives by this procedure has proved not to be straightforward and a note of caution needs to be sounded for possible future applications. The interception of the naphthalenyl anion **160** with amides gives rise to 1-acylcyclopropanaphthalenes **171** from simple addition−elimination to the carbonyl double bond (Scheme 29).[187] While acid opens the three-membered ring of these compounds (section IIIA), BuLi abstracts the remaining benzylic proton to give the corresponding enolates **172**, and these can be

Scheme 29



intercepted at oxygen with an appropriate nucleophile to give the exocyclic enol ethers **173a**−**g** as shown in Scheme 30.[187]

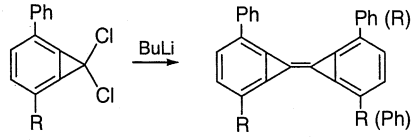
Scheme 30



It was noted earlier [section IIB, 4(b)] that methylidenemethano[10]annulene (**138**) adds dicyanoacetylene and that upon flash vacuum pyrolysis phenylacetylene is obtained likely via methylidenecyclopropabenzene (**139**).[124] However, parent **139** has not been isolated, and although other pyrolytic routes to provide it have been examined none have led to an isolable compound.[146,189,190] The application of modern low-temperature matrix procedures could prove valuable here.

At about the same time as Vogel's experiments,[124] Neidlein[185] showed that *gem*-dichlorocyclopropabenzenes **43** and **174** could be converted into their carbene equivalents that undergo dimerization to provide bicycloproparenylidenes **175** and (*E*/*Z*)-**176**, respectively. An attempted extension into the cyclopropa[*b*]naphthalene series from **46**,[79] the benzo analogue of **43**, resulted in a deep red colored material that displayed the characteristics of the sought after bicycloproparenylidene, but it was too unstable to allow for isolation and characterization.[191] Attempted syntheses of analogues of **175** from reaction of anion **160** with cyclopropenones (cf. Scheme 28) have failed, but intervention of the desired compounds appears likely and experiments to confirm this are underway.[176,191]

A notable limitation to the Peterson olefination procedures of Schemes 28 and 29 lies with the instability of oxocycloproparenes (section IID). Thus, an "inverse" silyl-Wittig reaction that uses a cyclo-

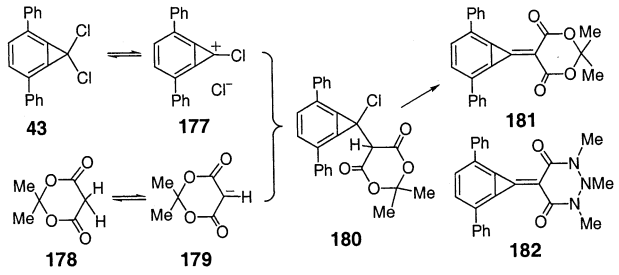


43, R=Ph
174, R=2-thienyl

175, R=Ph
176, R=2-thienyl

proparenone and a α silyl anion (that would become the exocyclic center) cannot be used. Nonetheless, the problem is not insurmountable, at least in part. Very recently, Halton and his group[188] have employed the cycloproparenyl cation **177**, derived[192,193] from the *gem*-dichloro-substituted **43**, and allowed it to react with an active methylene compound in the presence of base. The results, while preliminary in nature, clearly demonstrate that cation−anion pairing is followed by in situ ejection of HCl and formation of the desired olefin (Scheme 31). Thus, coupling of

Scheme 31



cation **177** with anion **179** from Meldrum's acid[194] (**178**) leads, via the nonisolable **180**, to alkene **181** (μ 5.1 D), but in a meager 22% yield. At the time of writing, the use of Meldrum's acid and *N*,*N*-dimethylbarbituric acid (to give **182**) are the only methylidene compounds that have been assessed.

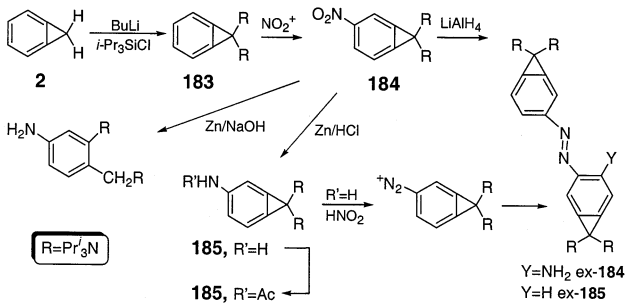
III. Chemistry of the Cycloproparenes

The chemistry of the cycloproparenes is dominated by the influence of the high strain energy for which theory[195] and experiment[24] agree as ca. 68 kcal mol^{-1}. Calculation[195] and experiment[196] also concur that the HOMO (b_1) of **2** is distributed between the bridge (C1a−C5a) and C3−C4 bonds and that it is higher in energy than the a_2 orbital. Thus, **2** should react with electrophiles and in cycloadditions at the bridge bond, the latter with the cyclopropparene behaving as an electron rich dienophile in inverse electron demand reactions. For convenience, the chemistry of the cycloproparenes presented below is divided between reactions types while the behavior of the oxo- and alkylidene-cycloproparenes is grouped together in an independent section.

A. With Electrophiles, Nucleophiles, and Radicals

The ability of the cycloproparenes to undergo classical electrophilic aromatic substitutions is frustrated by the low stability of the three-membered ring which favors capture of an electrophile by the π framework and formation of a benzylic cation from ring opening. Hence, **2** and its derivatives generally react with acids[197] and with halogens[2,63] to give benzyl derivatives as the major reaction products. If, however, the otherwise highly reactive three-membered ring is stabilized kinetically with bulky substituents then electrophilic aromatic substitution is recorded.[198] Thus, bis-silylation of **2** employing the bulky chlorotris(isopropyl)silane provides the sterically demanding disilane **183**. This, in turn, is nitrated at C-3 with 67% HNO_3 to give **184** in a yield of 58%. The site of attack is fully compatible with the location of the HOMO and the product yield can be improved upon by use of ultrasonic irradiation.[199] The steric protection present also allows for a range of transformations of the nitro-substituted product as shown in Scheme 32 that include reduction (with

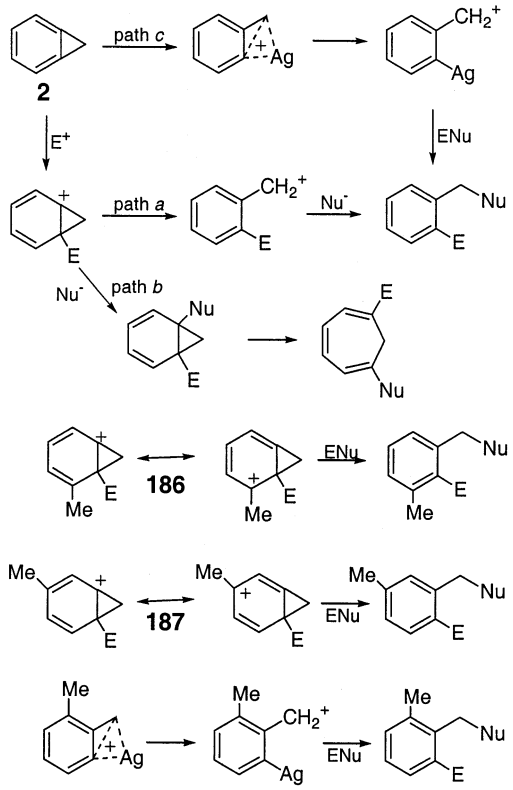
Scheme 32



and without ring opening) and diazotization of the ensuing cycloproparenylamine **185** (R′ = H); even an azo-coupled product has been obtained.[198] Eckert-Maksic[200] and co-workers have assessed by theory (HF/6-31G* and single point MP2(fc)/6-31G*//HF/6-31G* procedures) the possible Wheland intermediates in the reaction of **2** with H^+ and these concur with capture of the electrophile at C-3. The results are used to support Mills-Nixon[201] bond localization (see section V) in the direction indicated in **2**, and they have been coupled with comparable studies on as yet unknown C-1 heteroatom analogues.[202,203]

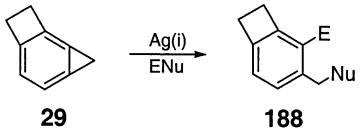
When sterically unencumbered, the cyclopropparene three-membered ring is opened by simple acids[197] and with halogens[2,63] in what is now recognized as a highly efficient benzylating reaction. The reaction could proceed by either opening the three-membered ring σ bond directly, or via initial capture of the electrophile by the aromatic π framework at C-1a. The best explanation[23] involves π capture of the electrophile (E^+) at the bridge bond followed by disrototory electrocyclic cleavage of the cyclopropyl cation thus formed (path *a*, Scheme 33). Subsequent interaction of the cation with nucleophile accounts for the observed product(s). The regioselectivities observed with 3-chloro-,[53−55] and 2- and 3-methylcyclopropabenzene,[63] are consistent with this pathway and demonstrate that capture of the electrophile at the bridge by the π framework preferentially provides the more stable of the two possible Wheland intermediates (cyclopropyl cations). Thus, the 2-methyl derivative gives *meta*-xylenes via ion **186** while the 3-isomer (and the 3-chloro analogue) also gives *m*-xylenes, but via ion **187** (Scheme 33). Furthermore, any capture of the cyclopropyl cation prior to ring

Scheme 33



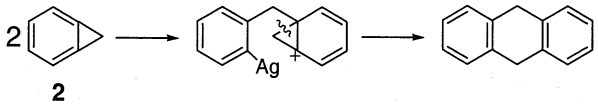
opening will result in the norcaradiene-cycloheptatriene equilibrium (path *b*, Scheme 33) as is observed[2,204] in the iodination of **2**. The formation of 1,6-disubstituted cyclohepta-1,3,5-trienes dominates under photochemical conditions with fluorescent light (>400 nm) and an equivalent radical pathway is presumed (see below).

The electrophilic opening of the three-membered ring of a cycloproparene is mediated by metal ions, and the use of Ag(I) has provided an especially efficient method of benzylation.[10,18,19] Thus, the silver-(I)-catalyzed reactions of **2** (and **6**) with alcohols, amines, and thiols proceed readily at 0 °C in aprotic media to give the corresponding benzyl derivatives in excellent yield.[19] In fact, the opening of a cycloproparene to a benzyl methyl ether provides a convenient transformation to confirm the presence of the cycloproparene[205] and was used for heat of formation and strain energy measurements.[24] The mechanism of these reactions most likely involves interaction of the metal ion with the strained σ bond coupled with ring cleavage and nucleophilic capture of the benzyl cation thus formed (path *c*, Scheme 33). The various regioselectivities are explicable in terms of the arguments advanced by the Garratt[63] and Billups[206] groups as discussed above. Thus, for 2-methylcyclopropabenzene the reaction yields *o*-xylenes since the incipient *ortho*-substituted benzylic cation is the more stable (Scheme 33). With ring-fused cycloproparenes, the more highly strained they are the more highly regioselective becomes the Ag(I) opening; angular cyclobutacyclopropabenzene **29** opens to give **188** regiospecifically, and the results obtained with this and a range of other derivatives are indicative of silver ion capture by the external σ bond of the three-membered ring.[63,206]



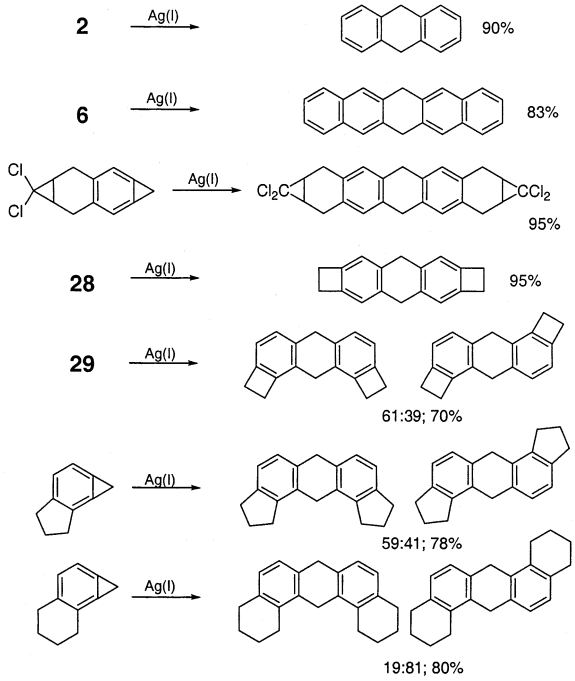
Silver(I) also promotes the addition of alkenes, alkynes, allenes, and conjugated dienes to cyclopropabenzene as has been discussed earlier,[15] and this ion, Cu(II), and Hg(II) have been used in the dimerization of **2**.[101,207,208] Nonetheless, it is the use of Ag(I) in the linear dimerization of the cycloproparenes that now commands most attention.[100,101,103,209] In 1974, Billups[207] showed that Ag(I) effected smooth dimerization of **2** to 9,10-dihydroanthracene. The formation of linear rather than angular (9,10-dihydrophenanthrene) dimer from **2** is dictated by electrophilic addition of the Ag(I)-complexed cycloproparene to the second molecule of reactant as discussed above and shown in Scheme 34. From this type of

Scheme 34



reaction, usually carried out in dry chloroform employing the soluble silver tetrafluoroborate salt, a range of dimers has been obtained.[100,101,209] As shown in Chart 2, product yields are generally excellent and

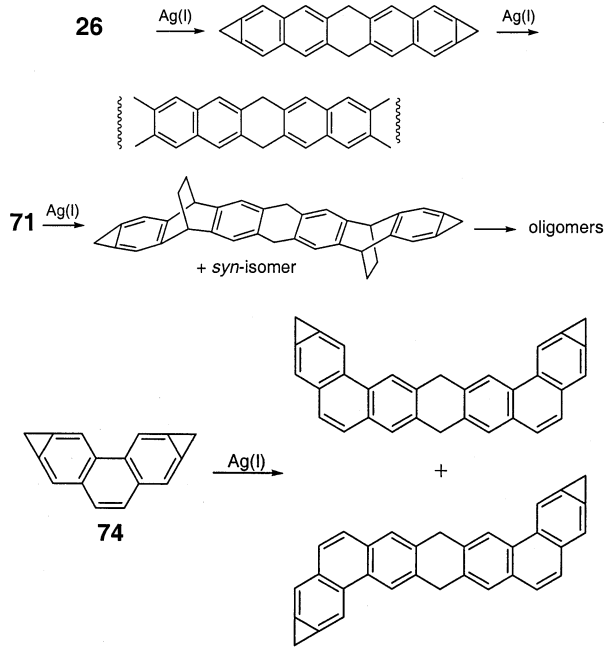
Chart 2



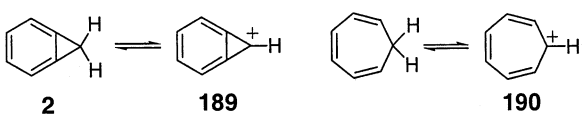
the regioselectivity is high. The products are themselves easily oxidized to the corresponding acenes.

More interesting still is the application of the Ag-(I)-reaction protocol to the dicycloproparenes as it provides for oligomerization.[100,101] Treatment of dicyclopropanaphthalene **26** with silver tetrafluoroborate gives rise first to dicyclopropadihydropenta-

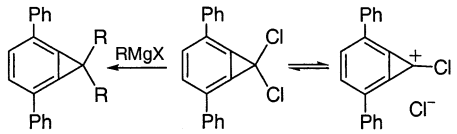
cene that can be isolated before oligomerization takes place. In like manner, the novel **71** dimerizes to what is thought to be predominantly the *anti*-isomer.[100] In the case of dicyclopropa[*b,h*]phenanthrene **74** the dimerization takes only five minutes and prolonged reaction gives rise to zigzag oligomers but not to macrocyclic assemblies.[101] In all cases examined the oligomers precipitate from solution as the chain length increases, for as yet there is no suitably functionalized dicycloproparene that could give rise to a soluble oligomeric product.



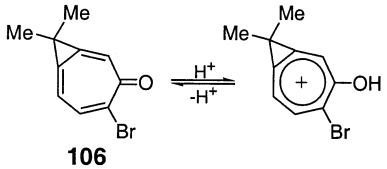
Removal of an anion from C-1 of a cycloproparene by interaction with a suitable electrophile has provided evidence for the existence of the cyclopropparenyl cation. Simple Hückel calculations from 50 years ago[13] and ab initio calculations[210] of 1992 agree that the resonance energy of the cyclopropabenzenyl cation **189** will be higher than that of the cycloheptatrienyl (tropilium) ion **190**. The latter places an additional 1 kcal mol^{-1} on the enthalpy change in transforming **2** to its derived cation (190.9 kcal mol^{-1}) compared with the cycloheptatrienyl counterpart (189.9 kcal mol^{-1}). Müller has shown that **2** reacts with triphenyl tetrafluoroborate to give **189** via hydride transfer some 5 times more slowly than cycloheptatriene;[211] the reaction of mono-deuterated **2** exhibits a kinetic isotope effect of 7.0.

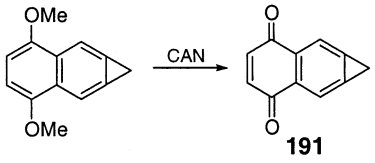


Upon treatment with antimony pentachloride the *gem*-dichlorocyclopropabenzene **43** ionizes and the salt **177** is isolated.[192] Indeed, ionization of a range of C-1-halogen substituted cycloproparenes is implicit in the chemical reactivity recorded[81,88,193,212] as has been adequately discussed in earlier reviews.[4,10,21] Suffice it here to note that the C-1 chlorine atoms of **43** can be replaced upon reaction with, e.g., Grignard reagents to provide *gem*-dialkylcycloproparenes.[213]



Upon exposure to trifluoracetic acid, cyclopropatropone **106** captures proton and gives the only known cyclopropa-fused nonbenzenoid aromatic ion, viz. the corresponding tropylium ion.[106] That the ion is present in solution is evidenced by a downfield shift of ca. 0.4 ppm in all the ring proton resonances. Unfortunately, the sample decomposed during an attempt to acquire the ^{13}C NMR spectrum. Here it is clear that despite the facility for opening of the three-membered ring by proton capture, it is kinetic control to generate the cyclopropa-fused cycloheptatrienyl cation that is recorded. As this example shows, the presence of a reactive functional group can target reagents and direct reactivity away from the strained ring. A further example is provided by the oxidative demethylation of 3,6-dimethoxycyclopropa[*b*]naphthalene with cerium(IV) ammonium nitrate (CAN).[64,65] Here, enedione **191** is formed in high yield as the first example of an isolable cyclopropaquinone capable of further functionalization into its anthraquinone analogue (see below).[214,215]

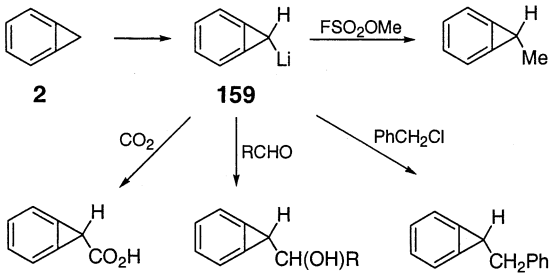




The transformation of a cycloproparene into a C-1 anion has been discussed already, as it is this species that forms the essential progenitor to silyl derivatives en route to the alkylidenecycloproparenes (section IIE). The earliest recorded abstraction of a cyclopropabenzenyl proton by base is attributable to Eaborn[216] who showed that upon metalation and silylation **2** gives **161** via (organolithium) **159** (Scheme 28). From base (HO$^-$) induced desilylation it was shown that the pK_a of **2** is ca. 36 since the desilylation proceeds some 36 times more rapidly than from benzyltrimethylsilane;[216] STO-3G calculations[217] give a value of 33 and it is clear that **2** (and its simple homologues) are more acidic than toluene (and the 2-methylarenes) in solution.

The existence of anion **159** has been confirmed from generation and spectroscopic observation in solution[218] and, more recently, in the gas phase.[219] The solution studies of Szeimies and Wimmer[218] involved proton abstraction from **2** with BuLi and

Scheme 35

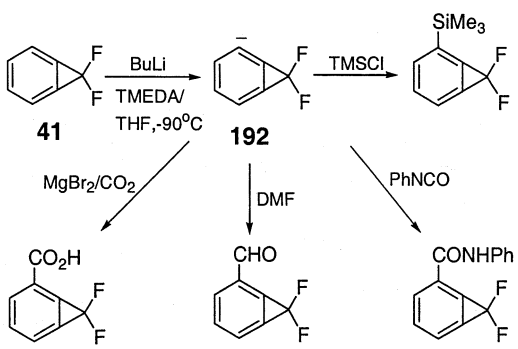


subsequent nucleophilic capture with a range of electrophiles as shown in Scheme 35. Deprotonation of **6** complexed with chromium tricarbonyl has also been effected and the resultant C1 anion intercepted by methyl iodide to give an epimeric mixture of complexed 1-methyl derivatives (see Scheme 45 below).[166] The recent gas-phase studies have allowed for the thermodynamic stability of anion **159** to be assessed. The measured acidity of cyclopropabenzene (**2**) is $\Delta H^\circ_{acid} = 386 \pm 3$ kcal mol^{-1}. This value is some 34.5 kcal mol^{-1} *more acidic* than that for loss of a C-3 proton from cyclopropene and 4 ± 3 kcal mol^{-1} *less acidic* than toluene; the experimental findings were satisfactorily reproduced by ab initio calculations at the MP2(fc)/6-31+G(d)//HF/6-31+G(d) and MP2(fc)/6-31+G(d) levels of theory.[219] The increased acidity of **2** compared with cyclopropene is rationalized by interplay between the ability of the aromatic ring to alleviate an unfavorable 4π electron interaction within the three-membered ring and a pyramidalization of the C1 center which minimizes interaction between the nonbonding electron pair and the aromatic sextet.

The removal of a cycloproparene C-1 proton and subsequent capture of the ensuing anion by groups other than silyl derivatives has not been easy,[218] but recent reports have shown that acetyl and benzoyl derivatives can be obtained.[161,186,187] In particular, acyl derivatives **171** are available (section IIE, Schemes 29 and 30) and upon deprotonation they give the corresponding enolate ions **172**, which have been trapped as enol ethers **173**.

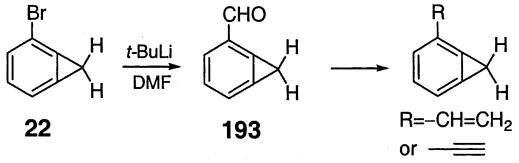
When there is no C-1 substituent capable of loss with its electron pair as in *gem*-difluoride **41** then strong base (BuLi in TMEDA/THF at −90 °C) abstracts the most acidic aromatic proton, namely, that at C-2 (Scheme 36).[220−223] The ensuing aryl anion **192** can then be intercepted by a wide range of electrophiles to give 2-substituted cyclopropabenzenes as

Scheme 36



has been demonstrated by Neidlein and co-workers;[223] selected examples are shown in Scheme 36. Furthermore, treatment of **41** with 2 equivalents of LDA interspersed with excess PhSSPh gives the 2- and 2,5-dithiophenyl derivatives, the latter being formed in low yield from sequential lithiation and anion capture.[220] More recently still, Logan[224] has shown that analogous lithiation at the arenyl C-2 site can be brought about with the C-1 methylene intact by using 2-bromocyclopropabenzene (**22**) with *tert*-butyllithium at −95 °C; the use of 2 molar equivalents of base ensures that 2-methylpropene and lithium bromide are the only side products. In the presence of DMF, 2-carbaldehyde **193** is formed in 84% yield, and this has been transformed into the 2-ethynyl and 2-vinyl derivatives (Scheme 37).[224]

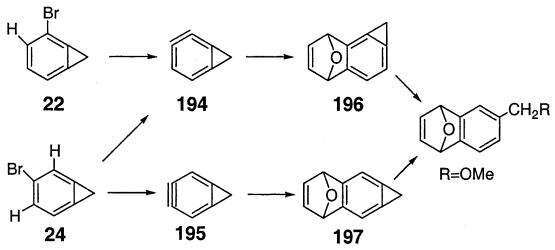
Scheme 37



Thus, aromatic substitutions at C-2 of the cycloproparenes are now comparatively easy to effect from **22**.

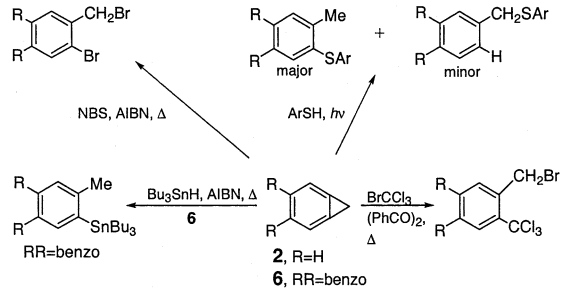
Traditional reaction of an aromatic substituent(s) remote from the three-membered ring has been demonstrated not simply for the nitro derivative **184** but also for the 2- and 3-bromocyclopropabenzenes **22** and **24** in their reaction with strong base (Scheme 38). These substrates undergo dehydrobromination

Scheme 38

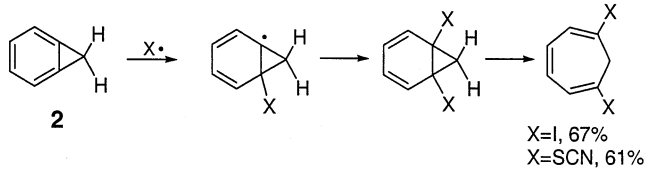


to cyclopropabenzynes,[195,205] which, despite their generation and trapping in 1983, retain their place as the most highly strained didehydrobenzenes so far recorded.[225] Treatment of **22** with *tert*-BuOK/NH_2^- in THF results in smooth dehydrobromination to the "angular" benzyne **194** that is intercepted by furan as Diels−Alder adduct **196**. In like manner, **24** provides both **194** and **195**, the former as the minor product of elimination. Again, the benzyne is trapped by furan but this time the symmetrical adduct **197** is the major product. Both adducts are opened to the same benzyl ether with Ag(I)/MeOH. Theoretical studies at the 3-21G*//3-21G level[195] place the heats of formation and strain energies of these benzynes as **194**: ΔH°_f 195; SE 175 kcal mol^{-1}; **195**: ΔH°_f 190; SE 170 kcal mol^{-1}. The lower stability of angular **194** by ca. 5 kcal mol^{-1} compared to linear **195** reflects a matching of distortions introduced by the small ring and the benzyne moiety on the aromatic nucleus of the latter but not the former.

Scheme 39



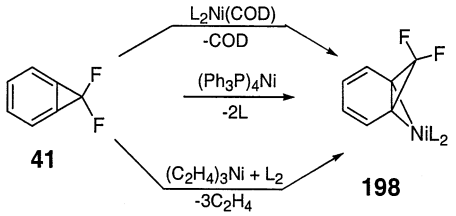
In reactions with radicals, the cyclopropabenzenes generally undergo opening of the three-membered ring as shown by the products of Scheme 39.[226] Here it should be noted that the ring openings, e.g., with PhSH and Bu_3SnH, give aryl-substituted product as major product with an orientation precisely the opposite to that of classical thermal chemistry. Despite these observations, Okazaki and co-workers[227] had earlier shown that the addition of iodine and thiocyanogen to **2** under photochemical conditions leads to 1,6-disubstituted cycloheptatrienes in good yields such that the reaction has provided for much use of **2** in synthesis.[123,204,228] In these reactions radical addition is thought to take place across the bridge bond to give a 1,6-disubstituted norcaradiene that opens to the preferred valence bond isomer, but smaller amounts (to ca. 30%) of α,*o*-disubstituted toluenes are still formed. There are no examples of comparable additions across the bridge (C1a−C7a) bond of naphthalene **6**, likely because of the high-energy orthoquinodimethane intermediate that would be required. Attempts to generate C-1 radicals from alkylidenecyclopropabenzenes have been without success.[226]



B. With Transition Metals and Related Complexes

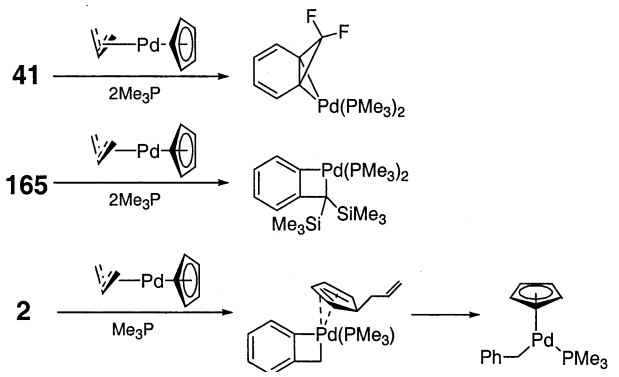
It is some 15 years since the first example of metal complexation across the strained bridge bond of **2** was recorded. Wilke and his group at the Max Planck Institute for Coal Research showed that *gem*-difluorocyclopropabenzene (**41**) reacts with a range of nickel(0) complexes to give nickelabicyclobutanes—complexes with a propellane structure.[229] Thus, the reaction of **41** with $L_2Ni(COD)$ [L = Me_3P, Et_3P, or ethenebis(dicyclohexylphosphane)], $(Ph_3P)_4Ni$, or $(C_2H_4)_3Ni$ and either TMEDA or bpy gives rise to the propellanes **198** in yield from 61 to 93% (Scheme 40);

Scheme 40



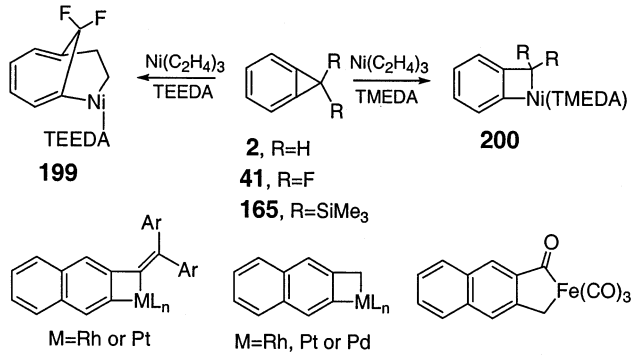
the crystal structure of bis(triethylphosphane) derivative confirmed the structure assignment. The complexes are stable at ambient temperature but revert to **41** in solution below −20 °C. A comparable addition takes place between **41** and (η^3-allyl)(η^5-cyclopentadienyl)palladium(0) in the presence of trimethylphosphane.[230] With the analogous C-1 disilane **165**, oxidative addition proceeds further to give ring opened palladacyclobutarene upon reaction with the palladium complex.[230] In contrast, the reaction employing unsubstituted **2** also proceeds to a palladacyclobutarene, but the species is unstable and ligand reorganization takes place with opening of the cyclopropabenzene ring; a benzylic palladium complex is isolated (Scheme 41).

Scheme 41



The nature of the metal ligands can have a marked impact on the outcome of reaction. For example, while **41** gives propellanes **198** as shown in Scheme 40, its reaction with tris(ethene)nickel(0) and TEEDA gives[231] the methano-bridged nickelanonatriene **199**. On the other hand, both **2** and disilane **165** give nickelacyclobutabenzenes **200**, the latter with both TMEDA and TEEDA (Scheme 42).[232,233] Nickelacy-

Scheme 42

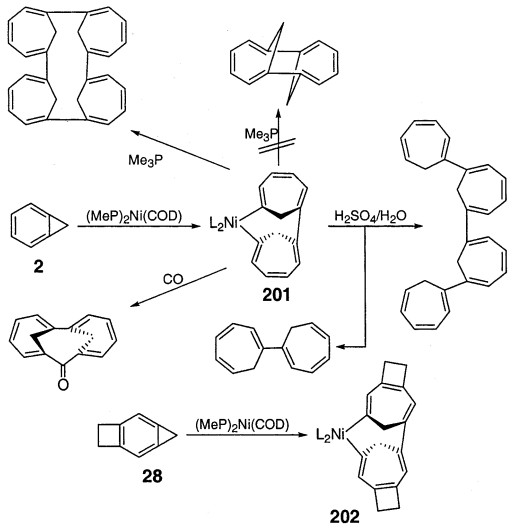


clobutarenes are also obtained from **2** with a range of other reagents,[232] and successful ligand exchange reactions have been recorded.[233] In the naphthalene series **6** has been shown to give metallacyclobutarenes with rhodium, platinum, and palladium reagents[234] and diarylmethylidenecyclopropanaphthalenes **168** likewise afford the rhoda- and platinacyclobutarenes shown in Scheme 42.[178] While iron complexes have not been assessed with the alkylidenecyclopropabenzenes, the earliest report of organometallic interaction with **2** was from diiron nona-

carbonyl; ring expansion and insertion of one CO ligand account for the metallaindanone obtained (Scheme 42).[235]

Cycloproparene coupling by use of organometallic reagents has been accomplished initially by the groups of Wilke and Neidlein.[236] Thus, when two molecules of **2** are added oxidatively to 1,5-cyclooctadienenickel(0) the bismethanocyclotridecahexaene **201** (L = PMe_3) is obtained (Scheme 43). In turn, the

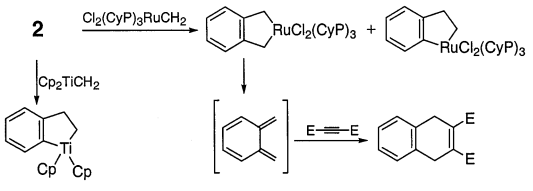
Scheme 43



Ni—C bonds of **201** are amenable to insertion reaction with subsequent reductive elimination and the range of compounds shown in Scheme 43 has been obtained. Precisely the same chemistry is displayed by the even more strained rocketene whereupon **202** is isolated in 79% yield.[237] Moreover, in an experiment in which **2** and **28** competed for the complex, all three of the possible products, viz. **201**, **202**, and the crossed product from **2** and **28** that contains one four-membered ring moiety, were obtained. The 4:1:4 ratio recorded is inconsistent with the bond localization hypothesis.

Both **2** and **6** have been reacted with metallacarbenes derived from ruthenium and titanium complexes.[238] The reactions with dichlorobis(tricyclohexylphosphine)methyleneruthenium form unstable 1- and 2-ruthenaindanes that decompose to styrenes and orthoxylylenes, respectively. The latter are trapped with dimethyl acetylenedicarboxylate as shown for **2** in Scheme 44. In contrast, the reaction

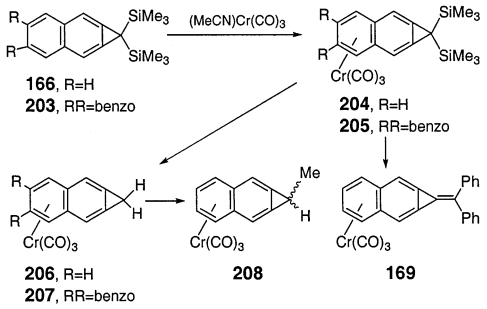
Scheme 44



of **2** with bis(η^5-cyclopentadienyl)methylidenetitanium leads to the moderately stable 1-titanaindane regiospecifically. With **6** this reaction shows a ca. 5:2 selectivity for the 1- over the 2-isomer, but the regioselectivities are not well understood.

In contrast to the above, the reaction of naphthodisilane **166** with triscarbonyl(acetonitrile)chromium(0) results in the ejection of acetonitrile and complexation of the metal with the ring most remote from the fusion site. Transition metal complex **204** is obtained and the cycloproparene remains intact (Scheme 45).[167,239] The same process pertains to the

Scheme 45

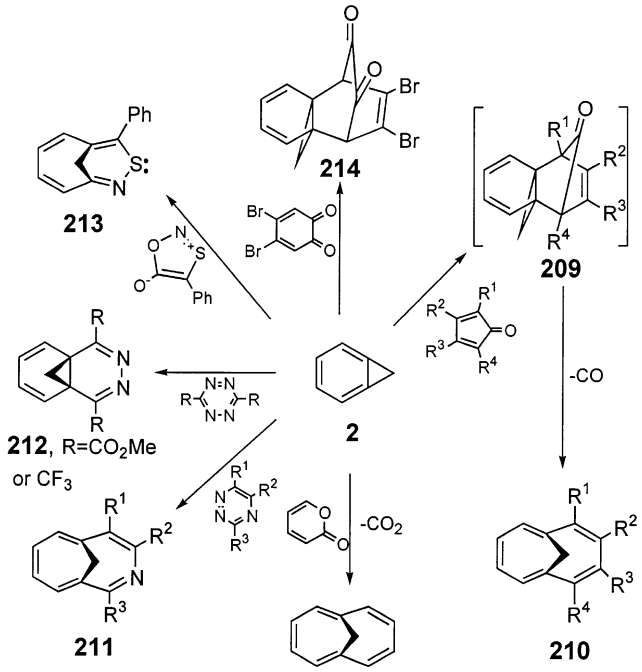


cyclopropa[*b*]anthracene analogue **203** and metal coordination is again to the site most remote from the three-membered ring.[167] It is felt that the steric protection at the C-1 center directs the metal to the remote ring as complexation is not achieved with disilane **165**, viz. for the cyclopropabenzene analogue.[166] The chromium complexed cycloproparenes **204/205** are sufficiently stable to allow for base-induced desilylation and the chromium tricarbonyl complexes **206/207** of the parent hydrocarbons **6/64** are isolated (Scheme 45). Moreover, transformation of **204** into the complexed alkylidene derivative **169** has been achieved using the standard Peterson methodology discussed earlier. Furthermore, **206** itself has been deprotonated (BuLi) to give anion that has been intercepted with iodomethane as epimeric 1-methyl derivatives **208**.[166] Comparable reactions of parent hydrocarbons **2** and **6** with the chromium reagent results in ring expansion to a cyclobutarenone.[167]

C. In Cycloadditions

As was noted earlier, the HOMO of **2** is located at the bridge and the C3—C4 bonds thereby enhancing electron density in the C1a—C5a bridge and creating within the cyclopropa rene an electron rich dienophile for use in inverse electron demand [2 + 4] {or [6 + 4]} cycloaddition reactions. This has proved to be the case and a range of Diels—Alder transformations involving **2** and electron-deficient dienes are shown in Scheme 46. The interaction of **2** with a range of appropriate cyclopentadienones[222] gives rise to unstable products that undergo cheletropic ejection of carbon monoxide and formation of the corresponding methano[10]annulene **210**. The reaction with 2,5-diethyl-3,4-diphenylcyclopentadienone has been monitored by ^{1}H NMR spectroscopy and the initial adduct characterized. The addition is *exo* to give norcaradiene **209** in which the carbonyl bridge and the three-membered ring are on opposite faces of the molecule.[222] In similar vein, α-pyrone provides methano[10]annulene after loss of CO_2.[197] Reactions with triazines[240,241] or tetrazines[242,243] likewise lead to addition—elimination, this time of dinitrogen. Addition of triazine gives a product is which the three-membered ring is opened, viz. the aza[10]annulene **211.** Strongly electron deficient triazines, e.g., R^1—R^3 = CO_2Et, add under normal conditions but when

Scheme 46

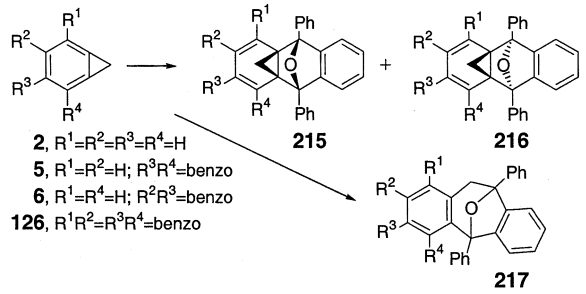


less activated, e.g., $R^1 = R^2 = H$; $R^3 = CO_2Et$, high-pressure conditions are required. In contrast, the addition of tetrazine dicarboxylate[242] or bis(trifluoromethyl)tetrazine leads to product **212** in the norcaradiene form. Indeed, **212** ($R = CF_3$) has provided for subsequent significant synthetic chemistry in which the distinct electron-rich cyclohexadiene and electron deficient diazadiene moieties are utilized independently.[243] The preparation of methano-bridged 10π electron nine-membered heterocycles, e.g., **213**, has also proved viable from use of **2** with appropriate mesoionic compounds[244,245] as initially signaled by the nitrile oxide additions of Nitta.[246] With 4,5-dibromo-1,2-benzoquinone, the crystalline adduct has been confirmed[247] as **214** in which the methano bridge and the dicarbonyl unit are anti.[248]

The formation of **209** and **214** is consistent with *exo* addition of the 4π electron diene to **2** as a 6π electron component. This raises the issue of bond localization in the cycloproparenes in the Mills-Nixon sense,[201] viz. as depicted by the structural representation of **2** used throughout, as this is nicely consistent with the stereochemistry of these cycloadditions. While discussion is deferred to section V, the orientation of addition is much more likely to be directed by steric constraints in reaching the transition structure than any in-built disruption to the σ or π framework.

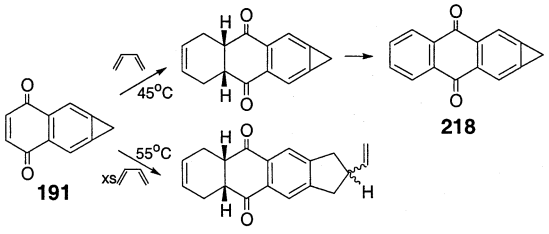
The essential cycloproparenes **2**, **5**, **6**, and **126** add various furans (Scheme 47). With diphenylisobenzofuran (DPIBF), **2** gives products from addition across both π and σ bonds in reactions that are solvent and time dependent.[249−251] In polar solvent such as chloroform addition is to the σ bond at ambient temperatures and **217** is isolated. However, in THF or THF/DMSO at room temperature addition to the π bond dominates and a ca. 5:1 mixture of *endo*-**215** (syn O and CH_2 bridges) and *exo*-**216** (anti bridges) (R^1-R^4 = H) is formed. Clearly, the classical Alder *endo* product **215** dominates as the products do not inter-

Scheme 47



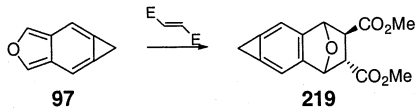
convert thermally at 60 °C.[250,251] At 80 °C, the yield of adducts increases markedly, but the proportion of *exo*-isomer is much higher. With the thermally unstable cyclopropa[*a*]naphthalene (**5**),[111] DPIBF trapping affords adduct that appears to be **215** ($R^1 = R^2 = H$; R^3R^4 = benzo) since the lowest field methylene proton is markedly deshielded (by the proximal O-atom) and appears at 3.36 ppm. No reaction of DPIBF with **6** takes place under the conditions that pertain to **2**.[250] However, at higher temperature (80°C) reaction does occur, but it avoids any disruption of the naphthalene π electron framework as addition is only across the three-membered ring σ bond to give the [3 + 2] adduct **217**.[252] The least stable of the simple cycloproparene hydrocarbons, **126**, was trapped by addition to furan as a mixture of *endo*- and *exo*- adducts **215** and **216** in a 3:2 ratio (see also Scheme 19).[114,115,117]

The use of furan as a trapping agent for the highly reactive cycloproparene-2,ω-diones **120** and **123** (Scheme 18), in which the three-membered ring is markedly more cyclopropene-like, has been discussed and the additions proceed to give mixtures of *endo* and *exo* isomers. Quinone **120** has also been intercepted from its addition across the 9,10-positions of anthracene [section IIB, 4(b)]. In contrast, naphthalene-3,6-dione **191** (formed by oxidative demethylation of the dimethoxy analogue[64,65]) adds dienes, including butadiene, across the enedione electron deficient double bond at room temperature.[214,215] A [$_\sigma$2 + $_\pi$2] addition to the three-membered ring competes upon heating above 45 °C. The reaction has provided for the first recorded homologation in the cycloproparene series, viz. from naphtho-**191** to anthraquinone **218** by way of cycloaddition and oxidative aromatization.[214] Furan neither adds across the π bond nor the three-membered ring σ bond even under high pressure, but isobenzofuran effectively adds to the former; the product epoxytetracenedione is air sensitive and decomposes under conditions designed to afford a cyclopropatetracene.[253]



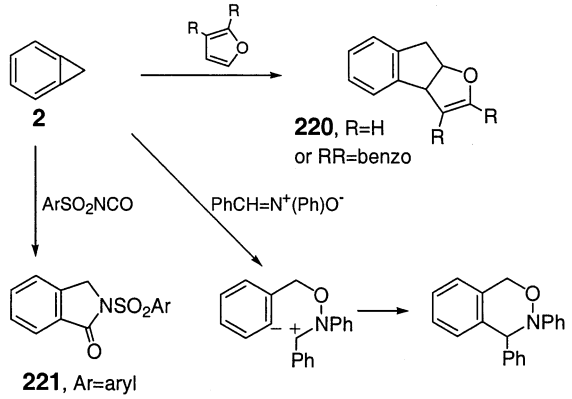
Reaction remote from the three-membered ring is also recorded for the nonbenzenoid 10π heteroaro-

matic **97** (X = O). Not surprisingly, dimethyl fumarate adds to the more electron rich furan moiety rather than the cyclohexadienyl entity (which would create a ring fused cyclopropene) and no [$_\pi$2 + $_\sigma$2] opening of the three-membered ring is recorded;[92,254] the result is formation of the ring fused cyclopropabenzene **219**. The reaction has been studied in detail and the first-order rate constants for this and a series other isobenzofuran/fumarate additions determined. The data show **97** to be some four times less reactive that parent isobenzofuran ($\Delta\Delta G^{\#} = 1.5$ kcal mol^{-1}) from which it must be concluded that there is no evidence to support bond localization in the π frame of the product cyclopropabenzene.



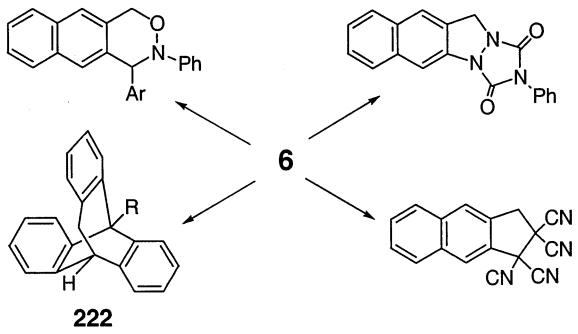
The examples of cycloaddition recorded above have shown that opening of the three-membered ring is energetically feasible. The [$_\pi$4+$_\sigma$2] addition of DPIBF to both **2** and **6** to give the oxygen-bridged heterocycles **217** have been alluded to above (Scheme 47).[249−251] With furan or benzofuran, Saito et al.[249] have shown that addition to **2** takes place in a [$_\pi$2 + $_\sigma$2] manner only to give indane **220** (Scheme 48).

Scheme 48



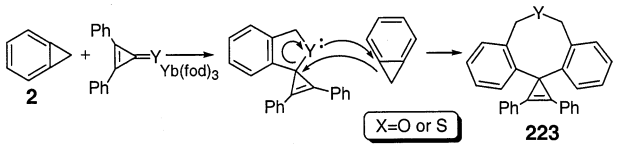
Under the conditions employed for the formation of **217** and **220**, the three-membered ring σ bond of the cycloproparene cannot give a "free" biradical as no dimerization to 9,10-dihydroanthracene is recorded; steric and polar factors are thought to dominate in these cycloadditions.[250] Whereas various dipolar reagents add to **2** to give products of π bond trapping, cf. **213** (Scheme 46), a range of electrophilic reagents lead to opening of the three-membered ring. Thus, the reaction of **2** with an arylsulfonyl isocyanates gives the isoindolinone **221**, and with *C*,*N*-electrophilic diphenylnitrone, the 1*H*-benzoxazine of Scheme 48.[255,256] Cyclopropa[*b*]naphthalene (**6**) adds a range of *C*-aryl-*N*-phenylnitrones in exactly the same way in reactions whose rates correlate with the Hammett σ values. Electron donation from the nitrone oxygen atom to the cycloproparene to give the zwitterionic intermediate of Scheme 48 has been proposed.[257] Cycloproparene **6** also adds *N*-phenyltriazolinedione,[250] tetracyanoethene,[252,258] and (as with **2**[259]) anthracenes[257] (Scheme 49), the last as a new and

Scheme 49



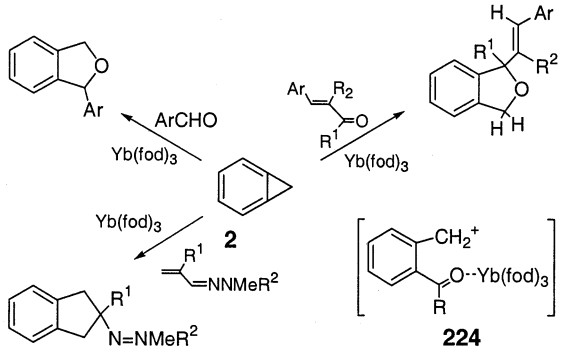
convenient method of preparing homotriptycenes **222** in yields that vary from 26% to almost quantitative. Zwitterionic intermediates again have been proposed and the nature and orientation of these is dependent upon which partner initiates the reaction.[250,252,257] What must be noted, however, is that it is only the regioisomers depicted that are formed.

A somewhat unusual outcome has been recorded for the reaction of two molar equivalents of **2** with both diphenylcyclopropenone and its thione analogue when catalyzed by Yb(fod)$_3$.[260] The dibenzooxocane product **223** (Y = O) is established from X-ray crystal structure, and it must result from openings of the three-membered rings; a plausible path is depicted.



Other uses of Yb(fod)$_3$ to catalyze reactions involving the σ bond of **2** with the formation of a range of interesting products has been developed by Neidlein and Krämer[261,262] and extended to **6** by Saito and his group.[263] Use of a range of α,β-unsaturated ketones and hydrazones leads to insertion of the heteroatom double bond into the σ bond of the cycloproparene and the range of products shown in Scheme 50 is

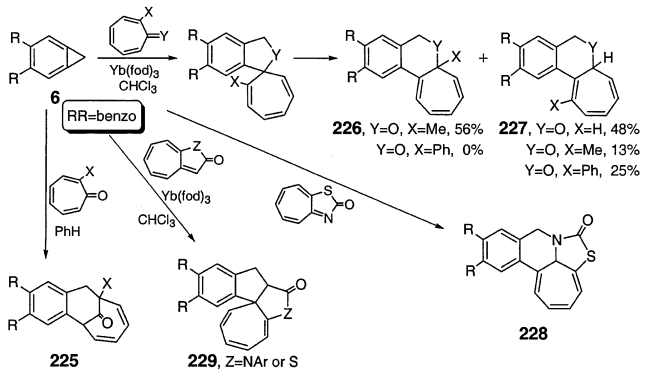
Scheme 50



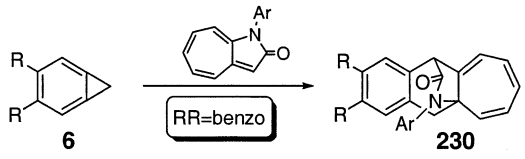
obtained, generally in high yield. It is thought that the reactions proceed by capture of the electrophilic sp^2 carbon by the arene to give a benzylic cation with heteroatom stabilization as illustrated by **224**.[261]

The work of Saito, admittedly restricted to **6**, has shown that tropones[263] and aza-, thio-, and thiaza-azulenones[264] are also able to react (Scheme 51). In

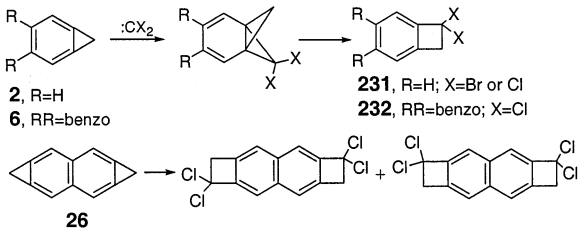
Scheme 51



benzene, and in the absence of catalyst, products **225** (18−45% yield) result from tropones in what is proposed as a concerted [$_{\sigma}2 + _{\pi}6$] addition to the strained bridge bond of **6** followed by rearrangement. With ytterbium catalyst the reactions transform to [$_{\sigma}2 + _{\pi}8$] additions to give **226** and **227** (identical for X = H). When X = Me **226** (Y = O) dominates, but it is completely suppressed in favor of **227** with X = Ph. The same type of product, viz. **228**, results from thiaza-azulenone, but ytterbium catalysis has no marked improvement on the 60% yield. In all probability, these catalyzed reactions pass through species equivalent to **224** that can close to a spirocycle and then ring expand to **226** or **227**. Aza- and thioazulenones add in [$_{\sigma}2 + _{\pi}2$] reactions in chloroform that are assisted by Yb(fod)$_3$ and give **229** in yields from 15 to 40%.[264] Use of aza-azulenones with **6** in benzene and *no* catalyst results in tetracycles **230**, and it is likely that these result from an initial [$_{\pi}8 + _{\pi}2$] cycloaddition across the cycloproparene bridge bond followed by ring expansion with relief of strain.[264] With iminotropones, **6** can give products analogous to **226**, but only in benzene with $AgBF_4$ catalysis. A catalyzed [$_{\sigma}2 + _{\pi}2$] addition involving the >C=N bond provides a spirocycle that ring expands as occurs for **226/227**. However, the major products of reaction are a 2-naphthylamide and tropone, and these must arise from preferential hydrolysis of the intermediate tropilium ion prior to its closure.[265]



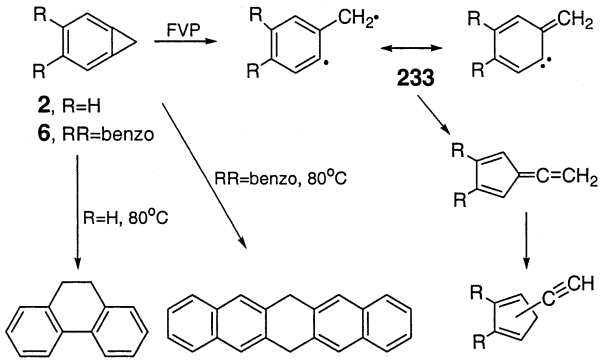
The cycloproparenes are also reactive toward dihalocarbenes and give the corresponding ring-expanded cyclobutarenes by what is likely an initial [2 + 2] cheletropic addition across the cycloproparene bridge bond. Cyclobutabenzenes **231** are isolated from **2** in near quantitative yield,[266] while the reaction with **6** has been performed only with dichlorocarbene; **232** is formed in 78% yield.[258] Dicyclopropanaphthalene **26** likewise adds dichlorocarbene (42%) to give regioisomers that were inseparable.[57] The interaction of **2** and **6** with metal carbenes has been noted above (see section IIIB).



D. Upon Thermolysis and Photolysis

Upon mild thermolysis at 80 °C cyclopropabenzene (**2**) undergoes dimerization to 9,10-dihydrophenanthrene.[2,197] Cyclopropa[*b*]naphthalene (**6**) ring opens under comparable conditions but gives the linear 6,13-dihydropentacene dimer and not its angular isomer (Scheme 52).[250] The same dimerization occurs

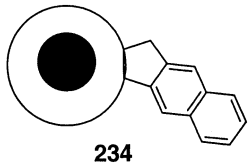
Scheme 52



with the benzodioxins **98** and **99**, but at low-temperature such that they elude isolation.[22,104] The coupling reactions most likely proceed by way of the ring opened α,*o*(1,3)-biradical that has now been characterized independently.[267] Photolysis of **6** in degassed cyclohexane (or pentane) leads to products of radical trapping. At 77 K the diradical (**233**; RR = benzo-fused) was persistent for several hours and the ESR spectrum (D/hc, 0.057; E/hc, <0.0002 cm^{-1}) was fully consistent with the product of σ bond homolysis. In studying electron transfer to **6** (potassium metal at −30°C in THF) a single detectable species was observed and identified as the anion radical of 6,13-dihydropenatcene.[268] *gem*-Difluorocyclopropabenzene (**41**) also opens to the 1,3-diradical in a reaction that has been the subject of physicochemical scrutiny.[269] Trapping experiments have shown the ground state to be a triplet and the lower limit for singlet−triplet splitting is at least 6 kJ mol^{-1}.

Under the more vigorous conditions of flash vacuum pyrolysis, dimerization is clearly avoided and ring opening to diradical/cyclohexadienylidene intermediate **233** occurs. Ring contraction of **233** to fulveneallene is followed by rearrangement to ethynylcyclopentadiene (Scheme 52).[270,271] Labeling studies have shown that the positional integrity of the atoms of **2** is maintained to fulveneallene but that automerization occurs in the subsequent rearrangement to alkyne. Cyclopropanaphthalene **6** behaves analogously giving (ultimately) the more highly conjugated of the possible products, namely, 2-ethynylindene.[272] Interception of intermediate **233** (R = H) has been

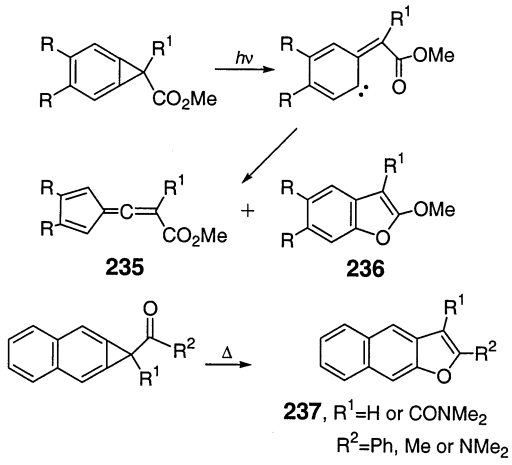
accomplished with ^{3}He-labeled C_{60} from reflux of **2** in benzene and adduct **234** characterized.[273]



234

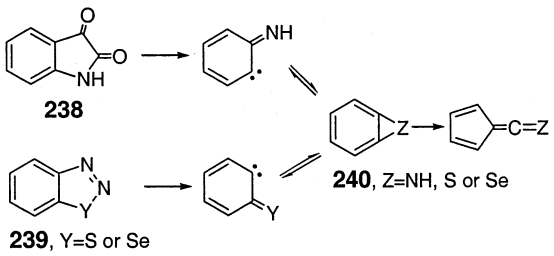
The involvement of carbenes equivalent to **233** in the photochemistry of the cyclopropabenzenes is well established. Photolysis of **2** gives rise to a mixture of dihydrophenanthrene and -anthracene[274] and the fact that allenes **235** are the major products from C-1 ester derivatives augers well for photo-Wolff rearrangement of the carbene (Scheme 53). The benzofurans **236** are minor product of photochemical but the major product of thermal rearrangement of these esters.[274,275] Analogous benzofuran products **237** are formed from thermolysis of the recently described 1-acyl and -amido derivatives.[187]

Scheme 53



That cyclopropabenzene−carbene rearrangement takes place upon FVP is strongly supported from results obtained with isatin **238** (Scheme 54). By using ^{13}C-labeled material a mixture of 1- and 2-cyanocyclopentadiene was obtained in which the label was scrambled between the cyano groups and the ring.[276,277] This is consistent only with equilibrium between the carbene and the (as yet) nonisolable benzazirine **240** (Z = NH) that then contracts to a fulveneallene. Independent studies of Schulz and Schweig[278] with indazoles **239** have led to the isolation and low-temperature IR spectroscopic identification of the thia- and selenacycloproabenzenes **240** (Z = S or Se). Earlier studies by these[279] and other workers[280,281] had been ambivalent on the involvement of the ring-closed species, and it seems clear that the precise reaction conditions employed are of the utmost importance.

Scheme 54



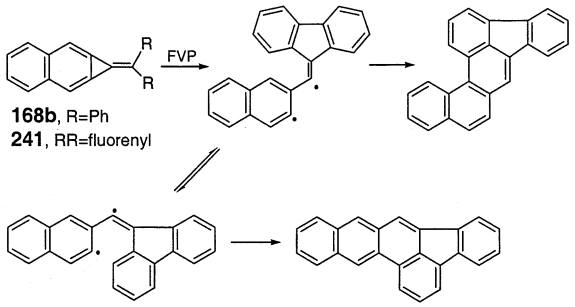
The thermal behavior of 1,1-dichloro-2,5-diphenylcyclopropabenzene (**43**) is governed by ionization−recombination. The *E*/*Z*-cycloheptatrienylidenes obtained from it[282,283] as well as the styrene products from thermolysis and photolysis of *gem*-dialkyl-substituted derivatives have been discussed adequately previously.[15]

E. Oxo- and Alkylidenecyclopropabenzenes

The chemistry of the oxocyclopropabenzenes is dominated by thermal ejection of carbon monoxide or, when a suitable reagent is employed, opening of the three-membered ring to afford, e.g., a benzoate ester as shown in Scheme 24. As discussed in section IID and depicted there in Figure 1, recent work has seen the incarceration of **144** inside a molecular container from which the decarbonylation and slow hydrolysis to benzoic acid have been studied.[143,144]

In contrast to the highly unstable nature of the oxocyclopropabenzenes, the alkylidene derivatives have remarkable thermal and photochemical stability. For example, heating **167a** or **168b** (R^1 = H; R^2 = Ph) in refluxing benzene for periods of several days effects no change.[284] However, this is counter to the instability of the parent **139** under the FVP conditions of its purported formation where ring opening and hydrogen shift give phenylethyne as the only hydrocarbon product isolated.[124] In fact, under FVP conditions the 8,8-diphenyl-**168b** and fluorenylidene-**241** derivatives do suffer σ bond homolysis leading to a mixture of polycyclic aromatic hydrocarbons as indicated in Scheme 55.[285]

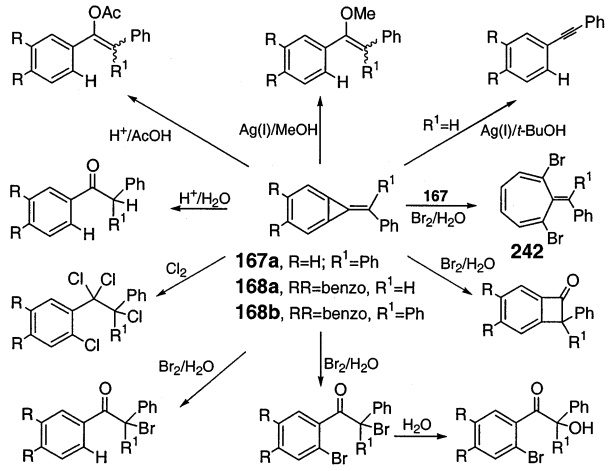
Scheme 55



The behavior of the exocyclic olefins to electrophiles and nucleophiles still remains to be explored in detail as the only reports are the early ones involving phenyl-, diphenyl-, and fulvalene-containing compounds.[168,182,286] This chemistry has been discussed in detail quite recently,[17] and consequently only a synopsis is provided here.

With electrophiles, reaction is akin to that of the hydrocarbon progenitors in that a generally rapid and irreversible opening of the three-membered ring occurs.[168,286] The range of examples provided in Scheme 56 come from the early studies and it should be noted that the formation of cycloheptatriene derivatives **242** takes place from the benzene, but not

Scheme 56[a]



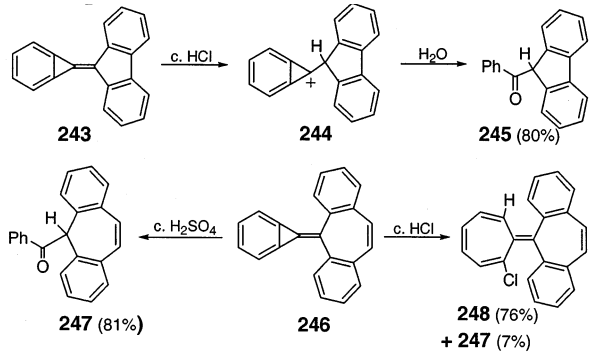
[a] Modified with permission from ref 17 (Copyright 1997 Thieme Medical publishers Inc.)

the naphthalene series. Under acid conditions, protonation of the exocyclic double bond appears to take place at the carbon remote from the cyclopropparene even when the attached aryl group is electron donating, e.g., *p*-anisyl, as an arylethanone is formed.[173] The simple aryl derivatives **167** and **168** undergo Ag(I)-catalyzed ring opening in methanol to give methoxystyrenes (Scheme 56) in ca. 75% yield in strict analogy to parents **2** and **6** discussed above (section IIIA). However, with the unsymmetrical phenylmethylidene derivatives **167a/168a** (R^1 = H) the product is accompanied by small amounts of arylethyne and this becomes the only isolable product from reaction in *tert*-butyl alcohol.[286] The formation of alkyne is easily rationalized from hydrogen transfer in the Ag(I)-complexed species and this again has analogy to **139** under the conditions of its formation. Under the conditions, favored for Ag(I)-catalyzed dimerization of the cyclopropparenes,[100,101,209] the exocyclic olefins are slow to react and then do not provide simple dimers.[165] It seems likely that the olefin substituents create sufficient steric compression to prevent an easy approach to the complex that is needed for dimerization, cf. that presented in Scheme 34 (section IIIA).

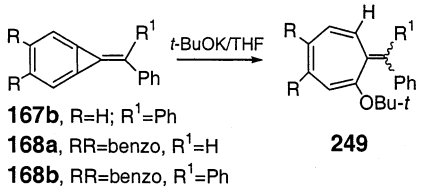
With fulvalene derivatives the impact of acids is again to open the small ring, but the direction of opening is not clear-cut.[168] The fluorene derivative **243** captures proton at the electron-sink site, the cyclopentadienylidene *ipso*-carbon, to give after workup, the ring opened 9-benzoyl derivative **245**. In contrast, the cycloheptatrienylidene homologue **246**, also polar *in the same direction* but less so (see section V), opens to give both benzoyl and bicycloheptatrienylidene derivatives **247** and **248** (Scheme 57); a route to **248** has been proposed.[168]

As the alkylidenecyclopropparenes are formed under strongly basic conditions, it is not surprising that they have good stability to such media. Nonetheless, prolonged exposure to base does result in the addition of nucleophile to the bridge bond as shown for *tert*-butoxide with **167/168**; heptafulvalenes **249** (R^1 = H or Ph) result from subsequent norcaradiene ring expansion.[182] The formation of enolate ions **172** from

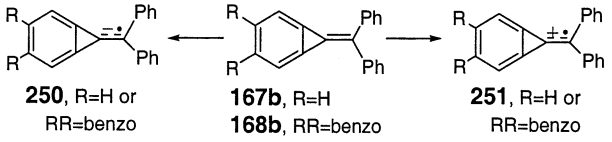
Scheme 57



1-acylcyclopropparenes and their subsequent capture as enol ethers **173** has been discussed (see Scheme 30, section IIE).[187]

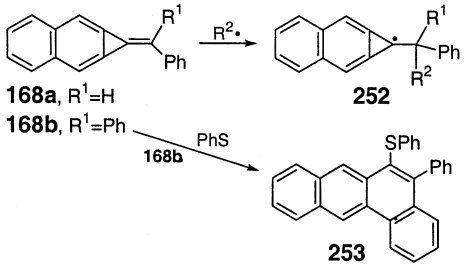


Electrochemical and spectroelectrochemical investigations have shown that each of **167b** and **168b** leads to a stable radical anion (λ_{max} 519 and 587 nm, respectively) and a quasi-stable radical cation in reduction and oxidation steps that are reversible.[287,288] It seems most probable that the cyclopropparene ring system is retained and structures **250** and **251** have been proposed.



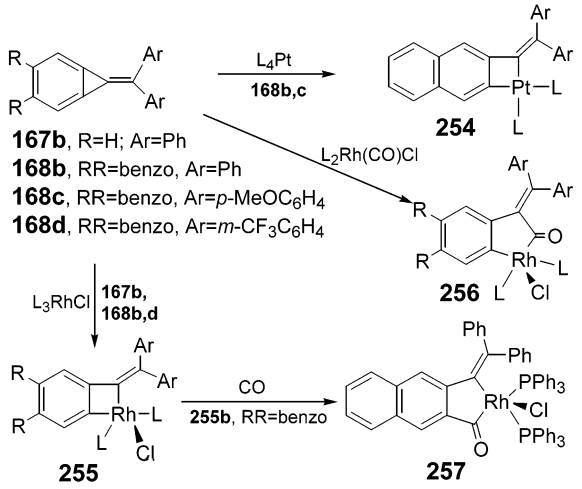
The facility by which **2** and **6** react with odd electron species suggests that the exocyclic olefins could well add a radical, and, if analogy to protonation were followed, a C1 cyclopropparenyl radical, e.g., **252**, would result. Despite the use of a variety of reagents under reaction conditions in which **167b/168b** are themselves stable, only complex mixtures of products were obtained.[226] With PhS•, **168b** gives the benzanthracene **253** but its formation does not demand the intervention of the sought after radical (Scheme 58).

Scheme 58



The only reactions between alkylidenecyclopropanes and transition metals have utilized 1,1-diaryl derivatives **167b** and **168b** with the group IX and X elements rhodium and platinum (Scheme 59).[178] The

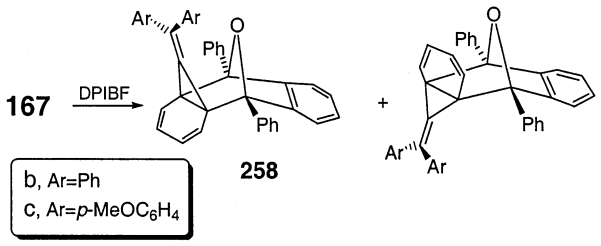
Scheme 59



outcomes are for platinacyclobutanaphthalenes **254** and, with chlorotris(triphenylphosphane)rhodium(I), rhodacyclobutarenes **255** in good yields and as stable crystalline compounds; the single-crystal X-ray structure of **255d** has been determined.[178] It seems reasonable to suggest that these four-membered ring systems arise by way of metallabicyclobutanes in analogy to the results presented in Schemes 40 and 41. When one phosphane ligand of the rhodium is replaced by carbon monoxide a different outcome is recorded. Oxidative addition of the metal is followed by insertion of CO and the rhodaindan-2-one **256** (X-ray structure for **256**; RR = benzo, Ar = Ph, L = PPh_3) is obtained. Treatment of the naphthocyclobutarene **255** (RR = benzo, Ar = Ph, L = PPh_3) with CO results in regioselective insertion into the weaker of the two Rh−C bonds and the isomeric rhodaindan-1-one **257** is the major product at low temperatures. The formation of chromium tricarbonyl complex **169** (section IIE) has been noted,[166] but its formation is by base-induced removal of the C-1 disilyl functionality and not from complexation of the diphenylmethylidene derivative itself.

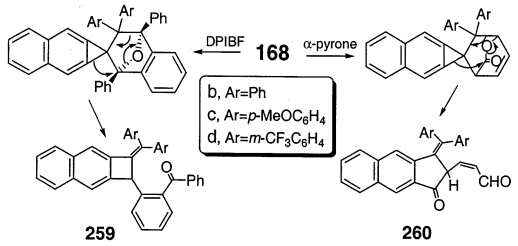
Cycloaddition chemistry of the diarylalkylidenecyclopropanes has received attention[289−291] and the behavior easily differentiates the benzene **167** and naphthalene **168** series. For none of the compounds are additions easy to bring about but use of ethylene glycol is efficacious. In the benzene series, DPIBF is incorporated with addition exclusive to the *bridge bond*. The norcaradiene-bridged *endo*-adducts **258** shown in Scheme 60 are confirmed as products from X-ray crystallographic analysis of **258b**; no products attributable to reaction across the exocyclic double bond or the three-membered ring σ bond were detected.[289,290] In contrast, the naphthalene homologues **168** react somewhat more readily and both DPIBF and α-pyrone add, but only at the exocyclic double bond.[289,291] It is presumed that the spirocyclic intermediates so formed are too unstable to survive

Scheme 60



the conditions and ring expand with relief of steric strain to give the cyclobutarenone **259** and the indanone **260**, respectively (Scheme 61). These ob-

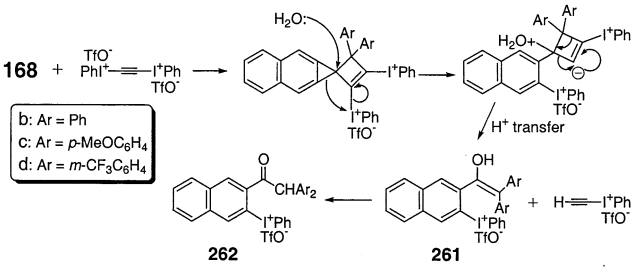
Scheme 61



servations match expectation as the cyclopropanaphthalene derivatives avoid high-energy orthoquinonoid structures equivalent to **258** that would result from loss of aromaticity in any addition to the bridge.[289] The reactions have been studied at the MP2/6-31G-(d)//HF/6-31G(d) and PM3 levels of theory, but the results were found disappointing. The PM3 calculations for the *actual* substrates used in the reactions did not mirror the experimental outcome but indicated bridge addition in both the benzene and naphthalene series.[289] This failure of theory is rather unexpected in view of the general success of ab initio calculations to reproduce reliably the transition state energies (and consequently regioselectivities, relative reactivities, etc.) of a wide variety of Diels−Alder reactions. The results of density functional calculations should prove more consistent and such outcomes are awaited.

With the highly electron deficient acetylenic(phenyl)iodonium triflates formal [2 + 2] addition takes place across the exocyclic double bond of cyclopropanaphthalenes **168b**−**d**. Again the spirocycles rearrange, perhaps as shown (Scheme 62), this time to

Scheme 62

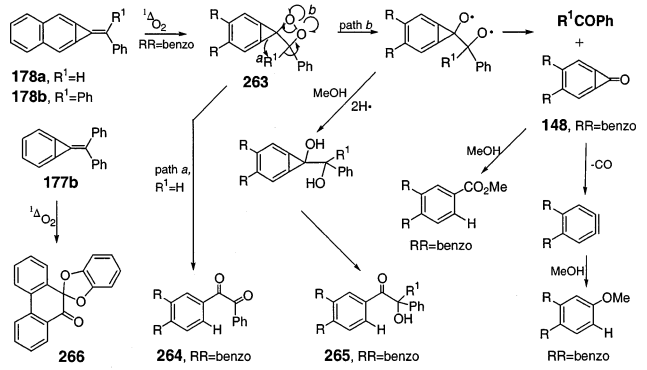


give 2,3-disubstituted naphthalenes **262**, and the involvement of enols **261** is confirmed from isolation of enol ether in the presence of methanol. Equivalent

chemistry has not been performed with cyclopropabenzene analogues **167**.

Photooxygenation of naphthalenes **168a** and **168b** with singlet oxygen (Rose Bengal sensitization) leads only to addition across the exocyclic double bond in what are likely $[_{\pi}2_s + _{\pi}2_a]$ cycloadditions.[182] It is not that the ensuing dioxetane intermediate **263** has been detected, but rather the nature of the reaction products that implicate its involvement. With an exocyclic hydrogen atom, **263a** ($R^1 = H$) ring opens with prototropic shift to give dione **264** (path *a*, Scheme 63). However, each of **263a** and **263b** opens

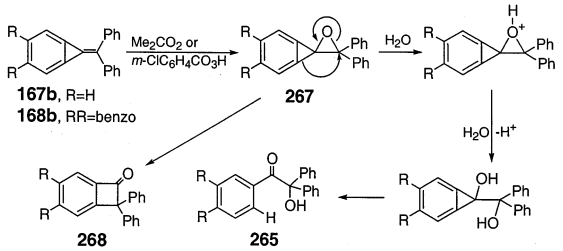
Scheme 63



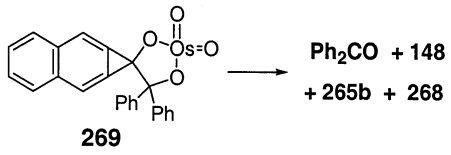
to provide a biradical (path *b*, Scheme 63). This can both cleave to a simple carbonyl compound (benzaldehyde or benzophenone) and cyclopropanaphthalenone **148**, and also abstract hydrogen atoms from the solvent to give an unstable diol that opens the three-membered ring to give hydroxyethanone **265**. Methyl 2-naphthoate and 2-methoxynaphthalene result from the opening of ketone **148** by methanol, and interception of 2,3-didehydronaphthalene from CO loss, respectively. The ester/ether ratios (but not product yields) recorded are independent of the initial olefins employed. The benzenoid counterpart **167b** does not react in the same way, rather the phenanthraquinone acetal **266** is obtained in low yield from a multicomponent mixture and its formation is not well understood.

Exclusive addition to the exocyclic double bonds of **167b** and **168b** is recorded for oxygen transfer from dimethyldioxirane. Irrespective of whether **167b** or **168b** is employed an oxaspiropentene **267** is formed as an unstable molecule that rearranges above 0 °C to the corresponding cyclobutarenone **268** (Scheme 64).[292] Low-temperature NMR monitoring has shown

Scheme 64



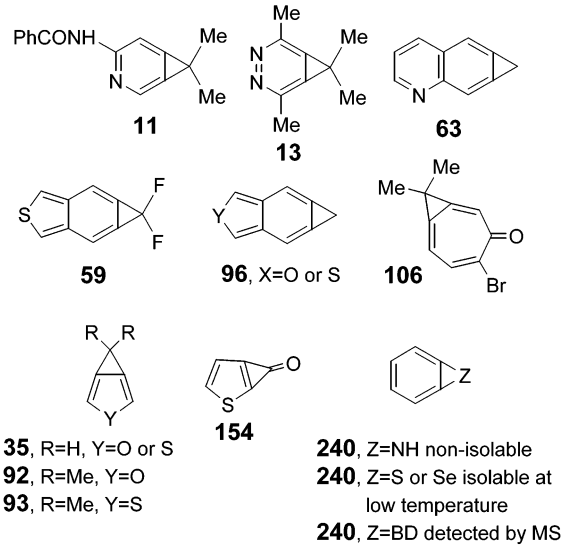
that epoxidation commences at about −50 °C to give spirocycles **267** that have been characterized from their ^{1}H and ^{13}C spectra prior to rearrangement setting in. These derivatives are the longest-lived oxaspiropentenes yet recorded[293] and illustrate that the stability imparted by the cycloproparene moiety augurs well for the detection of other reactive molecules as aro-fused derivatives. In the presence of water, epoxides **267** open both of the three-membered rings of the spirocycle to give the triarylhydroxyethanones **265**. When the epoxidation reaction is performed using MCPBA the initially formed **267** is protonated and the same acyloin results.[182] The presence of cyclobutarenone **268** is thus dependent upon a strictly anhydrous reaction medium. It is noteworthy that none of these reactions give any evidence in support of addition to the bridge bond with formation of an oxacyclobutarene (via an oxabicyclobutane) in analogy to the behavior of **2** and **6** with carbenes. Cleavage of the exocyclic double bond by more vigorous oxidizing agents also has been brought about. Thus, upon treatment with osmium tetroxide/sodium periodate, **168b** gives a range of products explicable in terms of the cyclic periodate intermediate **269** ejecting the organic moiety by pathways that encompass those of Schemes 63 and 64, but giving hydroxyketone **265b** as the major (65%) product.[182]



IV. Heteroatom and Related Ring Systems

The existence of heteroatom derivatives of the cycloproparenes has been alluded to in various parts of the foregoing discussion, but the specific structures are collected together here as Chart 3. The presence

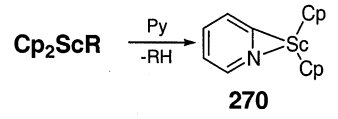
Chart 3



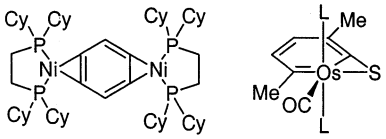
of cyclopropapyridine **11**[34] and -pyridazine **13**[35] (Scheme 4), -quinoline **63**[95] (Scheme 13) and isoquinoline **115**[112] are unexceptional save for the fact that they are heteroatom derivatives. The 10π elec-

tron nonbenzenoid cycloproparenes **59**[86] (Scheme 11) and **96**[92] (Scheme 16) are reactive molecules that give cyclopropabenzenes upon Diels−Alder cycloadditon across the heterodiene. Tropone **106** (section IIB 3b) is available and is protonated on oxygen.[106] The likely transient existence of the dimethyl-substituted thiophene **93**[68] (but not its oxa analogue **92** nor the parents **35**[66−68]) and the fact that cyclopropathiophenone **154** exists only in its ring open form under the conditions of formation[154] reflects the increased strain in the 5 atom 6π heteroaromatics compared with the 7 atom 6π analogues.

In contrast, the presence of a heteroatom in the three-membered ring is inferred from labeling studies for the benzazirine **240** (Z = NH) (Scheme 54).[276,277] However, with the larger bridging atoms S and Se, Schulz and Schweig have isolated and characterized the molecules **240 (**Z = S) and **240** (Z = Se) at low temperature.[278] Most recently, Kaiser and Bettinger[294] have generated benzoborirene **240** (Z = BD) from a crossed beam atom-molecule reaction of boron with perdeuteriobenzene. The product, detected by mass spectrometry, was calculated at the (CCSD(T)/cc-pVTZ//B3LYP/6−31 + G(*d*,*p*) level to be the most stable of the BC_6D_5 isomers. Moreover, the presence of an atom that can easily span the two adjacent site of a formal benzyne leads one now to expect isolation and characterization of such compounds. By way of illustration the scandium-bridged pyridine **270**[295] and the bis(nickelacyclopropa)benzene **271**[296] have been prepared and their crystal structures recorded. In similar vein, not only has a stable metallabenzyne been obtained[297] but also the thiacyclopropos mabenzene **272**, for which crystallographic data are available.[298]



270

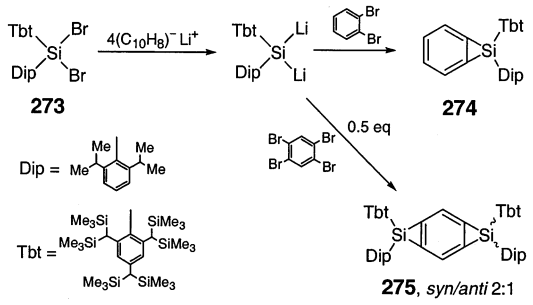


271, Cy=cyclohexyl

272, L=PPh_3

While the more traditional organic chemists may regard the last compounds as somewhat esoteric, this should not apply to the silacyclopropabenzenes reported by Tokitoh and his students.[299,300] From a series of elegant studies, initially with Okazaki to develop the sterically bulky protecting group "Tbt" (Scheme 65), reports have now appeared detailing the preparation of sila- and disilacyclopropabenzene **274** and **275** as shown. Treatment of the dibromosilane **273** with excess amounts of lithium naphthalenide in THF gives a silylenoid that couples with *o*-dibromobenzene and provides **274** in 34% yield. The compound is thermally stable in the solid state up to its melting point (257 °C) and because of the steric protection it is not opened by the action of methanol in refluxing benzene; the use of Ag(I) has not been assessed. This is the first stable example not simply

Scheme 65



of a sila- but of any 1-heteracyclopropabenzene derivatives. Use of 1,2,4,5-tetrabromobenzene with the same silylenoid provides a 2:1 mixture of the *syn*- and *anti*-isomers of the first recorded biscyclopropabenzene derivative **275**, but in the yield is low (1.5%). The structural parameters measured for **274** at −180 °C are shown in Figure 2 and have been compared

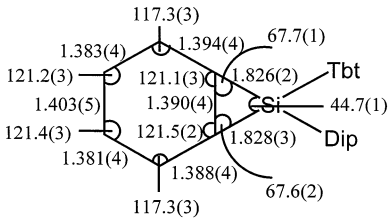
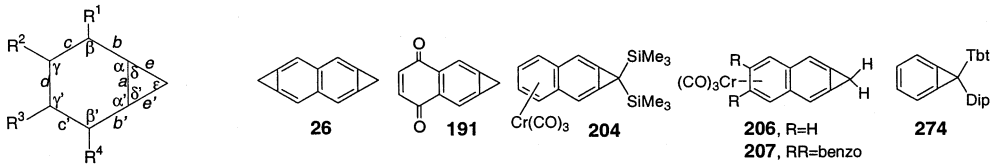


Figure 2. Bond lengths (Å) and angles (°) for **274**. Data taken from ref 299.

with computed values at the B3LYP/6−311(2d,p) level.[300] It is immediately obvious that the structure of **274** shows remarkably little variation in the benzenoid ring bond lengths as the mean value of 1.390 C is close to that of an unperturbed benzene bond; the bond angles are likewise close to 120°. This is in marked contrast to **2** itself (see section V). A range of unsubstituted (>SiH_2) silacyclopropabenzenes were the subject of an independent theoretical analysis[202] at the MP3(fc)/6-31G* level of theory prior to the isolation of **273** and **274**. The level of agreement is good for **273** and the results, which predict marked variations in bond lengths as the number of fused silicon-containing small rings increases, were taken to support bond localization in an anti-Mills-Nixon sense.

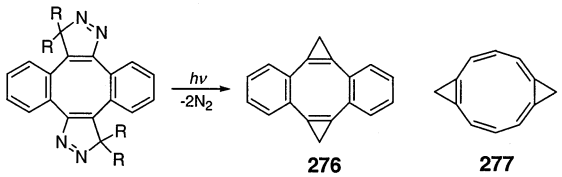
The fusion of a three-membered ring into the 4n conjugated cyclooctatetraene ring received attention as early as 1983. Dürr and co-workers[301] reported the synthesis and crystal structure of the biscyclopropa-[8]annulene **276**. Synthesis was achieved from a double ejection of dinitrogen from bis-pyrazole and the X-ray results showed an almost planar molecule with significant bond length variations in the fused benzene rings in analogy with the 1,5-diyne analogue. Compound **276** and a range of other cyclopropa-fused cyclooctatetraenes were addressed in MINDO/3[302] and PPP SCF-MO[303] studies and the adventitious use of cyclopropa fusion for planarizing nine- and ten-membered rings was pointed out.[304] Much more recently Schleyer has predicted[305] that the unknown dicyclopropa[*a*,*f*]cyclodecapentaene (1,6-dicyclopropa-[10]annulene) (**277**) will be planar with D_{2h} symmetry

Table 3. Structural Data of Selected Cyclopropanes Averaged on the Highest Molecular Symmetry



substituent(s)	*a*	*b b′*	*c c′*	*d*	*e e′*	α α′	β β′	γ γ′	δ δ′	ϵ	ref
$R^1 = R^2 = R^3 = R^4 = H$, **2**	1.334(4)	1.363(3)	1.387(4)	1.390(5)	1.498(3)	124.5(2)	113.2(2)	121.4(2)	63.6(1)	52.8(2)	308
disilane, **165**	1.336(3)	1.361(2)	1.401(4)	1.379(6)	1.541(1)	124.6(1)	112.9(2)	122.4(2)	64.3(1)	51.4(1)	308
$R^1 = R^4 = H$; $R^2R^3 = CH_2CH_2$, **28**	1.349(1)	1.385(1)	1.405(1)	1.402(1)	1.508(1)	126.3(1)	109.2(1)	124.4(1)	63.4(1)	53.2(1)	237
$R^1R^2 = CH_2CH_2$; $R^3 = R^4 = H$, **29**	1.351(3)	1.363(2) 1.368(2)	1.393(1) 1.401(4)	1.384(2)	1.507(2) 1.499(2)	120.0(1) 125.7(2)	116.3(2) 115.6(2)	123.7(2) 118.8(1)	63.1(2) 64.1(2)	53.4(1)	309
$R^1R^2 = R^3R^4 = CH_2CH_2$, **70**	1.363(4)	1.372(4)	1.411(3)	1.385(4)	1.506(4)	121.9(3)	117.7(2)	120.4(2)	63.2(2)	53.7(1)	309
$R^1 = R^4 = H$; R^2R^3 = benzo, **6**	1.375(2)	1.355(2)	1.414(2)	1.448(2)	1.503(2)	125.2(2)	113.6(2)	121.1(2)	63.2	54.4(2)	57
$R^1 = R^4 = H$; R^2R^3 = cyclopropabenzeno,**26**	1.360(3)	1.351(3)	1.437(3)	1.452(4)	1.499(3)	124.9(2)	114.8(2)	120.4(2)	63.2(3)	53.7(1)	57
$R^1 = R^4 = H$; R^2R^3 = benzoquinono, **191**	1.353(2)	1.370(2)	1.414(2)	1.416(2)	1.504(2)	124.9(2)	112.8(1)	122.2(1)	63.3(1)	53.5(1)	64
$R^1 = R^4 = H$; R^2R^3 = benzo-$Cr(CO)_3$ complexed disilane, **204**	1.384(14)	1.351(15)	1.451(15)	1.441(13)	1.510(15)	125.4(10)			62.7(7)	54.6(6)	167
$R^1 = R^4 = H$; R^2R^3 = benzo-$Cr(CO)_3$ complexed, **206**	1.368(7)	1.327(7)	1.436(6)	1.445(6)	1.490(8)	124.9(6)	114.(9)		62.7(7)	54.6(6)	166 167
$R^1 = R^4 = H$; R^2R^3 = naphtho[*b*]-$Cr(CO)_3$ complexed, **207**	1.36(1)	1.34(1)	1.43(1)	1.464(9)	1.48(1)	125.2(8)	114.0(6)		62.8(6)	54.5(5)	166
silacyclo-propabenzene, **274**	1.390(4)	1.391(4)	1.382(4)	1.403(5)	1.827(3)	121.4(2)	117.3(3)	121.3(3)	67.7(1)	44.7(1)	299 300

and exhibit properties consistent with aromaticity. The report of this or a derivative of it is eagerly awaited.



V. Physical and Theoretical Aspects

Early studies of the cycloproparenes were driven as much by the concepts of bond localization and the possible existence of the "cyclohexatriene" implicit in the Mills-Nixon hypothesis[201] as by the fascination of the novel strained ring system and the chemistry it could offer. Because of the suggestion that bond lengths in an aromatic ring could alternate because of the fusion of a small ring, much effort was expended to determine the single-crystal X-ray structures of most molecular types within the cycloproparene family. With the developments in computational capacity and the ease of data handling that it has brought, the advances in instrumentation, and the facility to operate at low temperatures, the period since the last review[10] has seen a number of elegant studies. These provide markedly more accurate data than the first (early) crystal structure determinations that demanded the presence of heavy atoms within the molecules.[306,307] The outcome is clear in that the bond lengths themselves do vary significantly but not in a simple alternation pattern. In terms of the Mills−Nixon hypothesis the variations are at best small and at worst insignificant, but without doubt their interpretation has been controversial! Table 3 contains the structural data for the important cycloproparene hydrocarbon derivatives **2**, **6**, **26**, **28**, **29**, **70**, the 1,1-bis(trimethylsilyl) derivative **165**, quinone **191**, and the chromium complexed species **204**, **206**, and **207**, together with those of sila derivative **274** for comparison purposes.

Much of the elegant work in providing accurate structural data for the cycloproparenes has come from Boese's group, not least because of the facility for crystal growth and transfer of the crystal to the diffractometer at low temperature, and it has received attention earlier.[4,310] As Table 3 shows the range of compounds assessed now includes all of the important small-ring fused cycloproparenes. It is clear from the data presented that there are marked bond length and interbond angle deformations principally about the sites of small-ring fusion. Thus, the cycloproparenes exhibit a reduction in symmetry with deformations occurring as a result of fusion strain. In all known derivatives the three-membered ring is essentially coplanar with the arene nucleus, as the tilt angle between the planes containing these rings is merely 1−3°. Interestingly, dicycloproparene **26** has its two three-membered rings each showing the same bending (1−3°) but in opposite directions.[57] The advances in ab initio basis sets has impacted upon the ability and ease of replicating the geometries and properties of known compounds, and predicting those

for derivatives that cannot be persuaded to offer a suitable crystal, as well those of as yet unknown analogues.[309] Calculations at the HF/6-31G(d,p) or MP2/6-31G levels replicate geometries well.[179]

Parent **2** and its C-1 disilyl-substituted derivative **165** show (apart from the lateral cyclopropene σ bonds, e/e') remarkably similar bond lengths and angles especially about the sites of ring fusion. In the benzene series, the bridge bond (bond *a*, Table 3) falls in the range 1.334−1.363 Å with the longest of these bonds in the tris-fused dicyclobutacyclopropabenzene **70**. Here, the increase in strain caused by the fusion of two additional small rings lengthens the bridge by 0.029 Å; the fusion bonds of the four-membered rings are also lengthened. In the naphthalene series, the range for bridge bond *a* is from 1.353 to 1.384 Å. In this context, it is worth recalling that the double bond in cyclopropene is 1.296 Å. The bonds adjacent to the small ring fusion (bonds b/b', Table 3) are also short. In the benzene series these are always *longer* (1.361−1.385 Å) than the bridge whereas in the naphthalene derivatives it is these bonds that are *shortest* (1.327−1.355 Å); naphthoquinone **191** is the exception, but then this compound is more in keeping with a benzenoid derivative. The bond angles about the fusion sites (angles α/α', Table 3) are widened (121.9−125.4°) save for the angular bis-fused **29** (α, 120.0°). In comparison, angle β is narrowed by as much as 10° (109.2−117.7°) and the most remote angle (γ) is widened slightly (120.4−124.4°) but always to a lesser extent than occurs for angle α. The angles ϵ and δ of the three-membered ring are each remarkably similar in all compounds studied with values of ca. 63.3° and 51.4−54.7°, respectively. The silacyclopraparene **273** exhibits similar trends, save for a bridge bond that is the same length as the adjacent bonds (1.390 and 1.391 Å) and an even more compressed sp^3 angle ϵ of 44.7° at the silicon atom.

The obtuse angle for C1−C1a−C2 is widened dramatically in all compounds from the 120° between any normal double bond substituents to a value in excess of 170°. It accounts for the ca. 0.02 Å shortening of the σ bond (bonds *e*) compared to that in cyclopropene. In the symmetrical **28** the obtuse angle is 170.3(2)°, in **2** 171.7(2)°, in the tris-fused **70** 174.9(3)°, but in the unsymmetrical **29** the bay region has the largest value so far recorded in any known compound, namely, 176.9(1)°; bond *b* connecting the two fused rings in **29** (1.363(2) Å) is shortened the most in the three derivatives **28**, **29**, and **70**. The values again serve to emphasize the distortions about the aromatic σ frame caused by small-ring fusion. The availability of these multiple small-ring annelated derivatives shows that in comparison with **2** and **6**, rocketene **28** has its internal bond angle at C-2 (angle β) markedly narrowed (from 113.0 to 109.2°). The three- and four-membered ring σ bonds are lengthened somewhat, but it is the bonds adjacent to three-membered ring fusion that are lengthened most (by 0.022 Å) in comparison to parent **2**. The impact of the three-membered ring fusion has been elegantly demonstrated by Boese using X−X deformation electron density maps. These show that the "bond path bond length", which follows the electron density contour between any two atoms, corresponds closely to that of the normal (unperturbed) bond length (1.395 Å) for a benzene bond. The shortened internuclear separation reflects induced strain[310] and a distinction between separation and bond path is justified. The phenomena are illustrated in Figure 3 for quinone **191** where the C1a−C7a

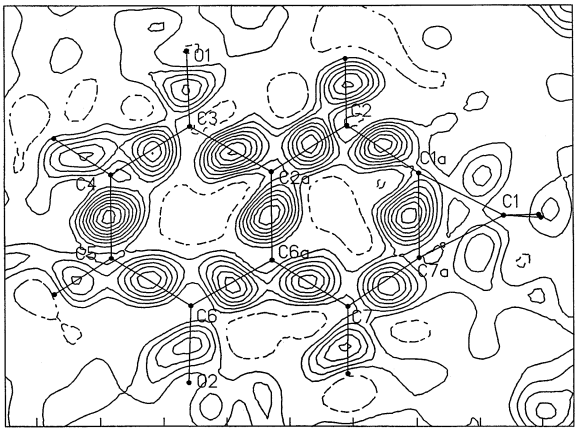


Figure 3. X−X difference electron density map of cyclopropa[*b*]naphthalene-3,6-dione (**191**) (contours every 0.05 e Å^{-3}) from *J. Chem. Soc., Perkin Trans. 1* **1996**, 1445−1452 (ref 64). Reproduced by permission of the Royal Society of Chemistry. Copyright 1996.

bonding electrons clearly implode into the benzenoid ring and even those of the more remote C2a−C6a bond are displaced toward the quinone moiety.

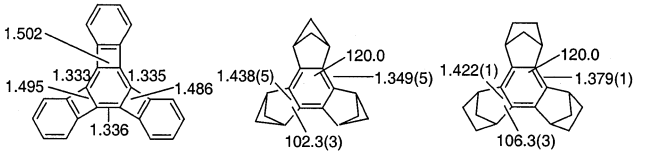
The sp^2-sp^2 bridge bond lengths in **26** provide a measure of the strain introduced into the naphthalene moiety by double three-membered ring fusion. The reduction of bridge distance *a* in **2** compared with benzene (0.062 Å) and in **6** compared with naphthalene (0.035 Å) reflects the greater facility for strain relief in the latter. In **26** the value (0.051 Å) falls between the two and indicates the increase in strain energies to ca. 120 kcal mol^{-1}.

The chromium-complexed cyclopropanaphthalenes **204** and **206** show that the subunit complexed to the metal has parameters that match well those of the complexed ring of tricarbonylnaphthalenechromium and this includes the central C2a−C6a bond (bond *d*, Table 3). The uncomplexed parts the structures compare favorably with those of mono **6** and dicyclopropanaphthalene **26**. The anthracene **207**, which remains the sole derivative of this ring system with measured crystallographic data, equates almost to a superimposition of the structure of cyclopropanaphthalene **6** on tricarbonylanthracenechromium. Most notable is the fact that the remote complexation has minimal impact upon the geometry of the fused cyclopropanyl moiety.

The range of structural parameters now available shows: (i) that the annelation of a small ring to benzene gives rise to "banana bonds" with the result that simple internuclear separations can be misleading, and (ii) that bond length alternation is not in excess of 0.025 Å (2.5 pm) compared with the parent arene.

The synthesis of ring-fused aromatics that display clear bond length alternation has been one of the

more pleasing achievements in recent years. The first clear case came from the work of Vollhardt[311,312] and showed tri(cyclobutadieno)benzene (**278**) to have endo and exo bond lengths in the central ring differing by ca. 0.160 Å (16 pm). Such a compound does not relate easily to the cycloalkabenzenes, and it is the derivatives fused to alicyclic rings that command most interest in this regard. These are illustrated by **279**[313] and **280**,[314,315] the first mononuclear benzenoid hydrocarbons with cyclohexatriene-like geometry. The bond alternation in **279** and **280** is much smaller than for **278,** but it is undoubtedly present and close to 9 and 4.5 pm, respectively. In **279** the deviations in the "benzenoid" bond lengths are more than 4σ more for the *endo*, and more than 4σ less for the *exo* bond compared to a normal hexa-substituted benzene. The molecule displays the ^{13}C resonance for these atoms at the typical aromatic position of 135.9 ppm. The geometries of **279** and **280** have been replicated by calculation at the HF/6−31(G) level and higher, but it is the density functional calculations that provide the closer fit.[316]



278, bond lengths in Angstroms

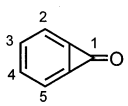
279, bond lengths in Angstroms, angles in deg.

280, bond lengths in Angstroms, angles in deg.

In comparison to **279** and **280**, the variations in the cyclopropparene aromatic bond lengths given in Table 3 range from 2 pm in silacyclopropabenzene **273** to ca. 12 pm in the chromium complex **206**. However, in *none* of these compounds is there *any evidence* for a bond alternation akin to that in the tris(bicyclo)-substituted benzenes **279** and **280**. Rather, there is a strain-induced shortening of the bonds about the sites of ring fusion. Even if one regards the bridge bond as lengthened (as it is compared to the π bond of cyclopropene) then the two adjacent short bonds are not matched with a shortened remote bond (bond *d*, Table 3).

Since the early discovery by Mills and Nixon that indane and tetralin showed enhanced positional selectivities in their brominations,[201] the properties of the cycloalkabenzenes have attracted attention. The impact of a small fused carbocyclic ring was found to direct electrophilic substitution to the β-position. This effect—the Mills−Nixon effect—was accounted for by partial π electron localization caused by fusion of the small ring. According to this, the bridge bond was proposed to have enhanced single bond character. In recent times, the presence or absence of a Mills−Nixon, or a reverse Mills−Nixon effect has been discussed for the cyclopropparenes in regard to selectivities in electrophilic aromatic substitution (in solution), in the derived cations and anions,[200,202,317−319] and in the analysis and interpretation of crystal structure data of ring-fused aromatics.[179,180,308,309,320,321] The concepts of strain induced bond localization (SIBL)[322−326] encapsulate the principles of the Mills−Nixon effect and a clear distinction between crystallographic measurements that pertain only to the σ framework and any strain induced effects that impact upon the π orbitals must be made. The discussions far surpass the scope of the present account and the reader is referred to recent reviews of the area by Shaik and Maksic and their respective co-workers.[317,327] Suffice it here to say that as far as the cyclopropparenes are concerned this author sees no meaningful evidence for bond alternation. What is significant is that the diatropic ring current of benzenes strained by annelation of cyclopropa-, cyclobuta-, and cyclobutadieno clamps now can be directly visualized from use of a reliable distributed-origin, coupled Hartree−Fock method.[328] When only saturated clamps are employed, as in the cyclopropa- and cyclobutarenes, the benzene ring current is essentially unchanged. Hence the theoretical base shows a clear disruption to the symmetry of the σ frame in a cyclopropparene that is not coupled in any way with a comparable disturbance in the π network.

NMR spectra of oxocyclopropabenzene (**144**) have been recorded for the free[142] and encapsulated (Figure 1) guest molecule.[143] The former were commented upon earlier[4] and the data, given in Figure 4, indicate



144

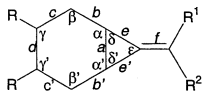
atom	*free*	*guest*
H2/5	8.28	7.05
H3/4	7.82	4.35
C1	154.9	149.7
C1a/5a	141.7	140.2
C2/5	117.9	116.9
C3/4	139.3	138.5

Figure 4. NMR spectral data for **144** recorded for [D_6]-acetone (free) and [D_8]-THF (guest) solutions. Data taken from ref 143.

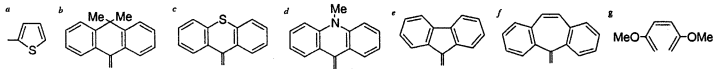
an upfield shift of 1−5 ppm for the guest with C2 as the least affected center. However, the structural parameters of guest **144**, while promised,[144] had not appeared at the time of writing.

Eleven of the alkylidenecyclopropparenes have been subjected to crystallographic analysis with three coming from the benzene series (Table 4).[17] The results show that the cyclopropparenyl moiety retains its essential planarity with the three-membered ring bent out of the plane of the aromatic unit by the same 1−3°. Bonds *c* and *d* remote from the fusion site are similar in length to those in the nonalkene parents. The differences lie in and about the three-membered ring. Low level HF/STO-3G calculations[179,330] provided a geometry for the unknown parent **139** some 15 years ago, but it is the more recent (1998) HF/6-31G(d,p) data[179] that are included in Table 4 for comparison purposes. The calculations show that methylidenecyclopropabenzene (**139**) is *less* strained than parent **2** by ca. 2 kcal mol^{-1} because of charge separation. The computed π and total charges indicate that **139** is polarized with a positive cyclopropparenyl moiety and a dipole moment (now) of 1.8 D to lie in the direction of the exocyclic center.[179] The HF/6-31G(d,p) results likely overestimate the magnitude of this dipole as judged from the measured polarity of many of the available derivatives[165] (Table 1, section IIE) where dipole moments fall in the range 1.0−4.3 D (the 9.1 D thienyl, entry 55, Table 1, is an exception); they can be oriented toward or away from

Table 4. Structural Data of Selected Alkylidenecycloproparenes Averaged on the Highest Molecular Symmetry



Substituent(s)	*a*	*b* *b'*	*c* *c'*	*d*	*e* *e'*	*f*	α α'	β β'	γ γ'	δ δ'	ε	Ref.
R=R^1=R^2=H, **139 – calc.** HF/6-31G(d,p)	1.347	1.382	1.3881	1.407	1.435	1.318	124.3	113.1	122.6	62.0	56.0	179
R=H; R^1=R^2=Ph, **167b**	1.355(4)	1.379(5)	1.384(6)	1.388(6)	1.433(5)	1.343(4)	124.0(3)	113.0(4))	123.0(4)	61.8(4)	56.4(2)	160
RR=benzo; R^1=R^2= *p*-Me$_2$NC$_6$H$_4$-	1.399(3)	1.352(4)	1.437(4)	1.431(4)	1.440(4)	1.346(3)	124.3(2)	114.4(2)	121.3(2)	60.9(2)	58.1(2)	164
RR=benzo; R^1=H; R^2=*p*-Me$_2$NC$_6$H$_4$	1.395(3)	1.346(3) 1.354(3)	1.433(3) 1.425(3)	1.440(3)	1.448(3) 1.443(3)	1.329(3)	124.3(2)	114.7(2)	121.3(2)	61.2(1)	57.7(1)	164
RR=benzo; R^1=H; R^2=2'-thienyl[a]	1.381(11)	1.400(12) 1.348(12)	1.462(12) 1.431(11)	1.498(11)	1.403(11) 1.415(12)	1.351(12)	119.0(8) 127.7(7)	120.8(8) 114.9(7)	114.7(7) 123.1(7)	61.1(6) 60.2(6)	58.7(6)	164
RR=benzo; R^{1}R^2=9-(10,10-dimethyl)-anthrylidene[b]	1.388(4)	1.352(3)	1.425(4)	1.445(4)	1.431(3)	1.352(4)	124.3(7)	114.8(4)	120.9(2)	61.0(1)	58.0(2)	180
RR=benzo; R^{1}R^2=9-thio-xanthenylidene[c]	1.384(5)	1.354(4)	1.431(4)	1.445(6)	1.433(5)	1.354(5)	124.7(3)	114.3(3)	121.1(3)	61.2(3)	57.7(3)	180
RR=benzo; R^{1}R^2=9-(*N*-methyl)acrydinylidene[d]	1.400(2)	1.355(1)	1.439(2)	1.444(2)	1.429(2)	1.362(2)	124.4(2)	114.5(1)	121.1(1)	60.7(1)	58.6(1)	180
RR=benzo; R^{1}R^2=9-fluorenylidene[e]	1.390(2)	1.362(2)	1.423(2)	1.451(2)	1.430(2)	1.346(2)	124.4(2)	114.3(1)	121.3(2)	60.8(1)	58.2(1)	179
R=H; R^{1}R^2=9-fluorenylidene[e] **243**	1.377(5)	1.385(4)	1.393(7)	1.410(6)	1.441(4)	1.338(5)	123.7(4)	113.5(4)	122.9(4)	61.4(3)	57.1(3)	179
R=H; R^{1}R^2= dibenzo-cycloheptatrienylidene[f] **246a**	1.371(2)	1.382(2)	1.399(2)	1.406(3)	1.438(2)	1.347(2)	124.2(3)	113.0(3)	122.8(2)	61.5(1)	57.0(1)	179
RR=1,4-dimethoxybenzo;[g] R^{1}R^2= dibenzocyclohepta-trienylidene[f] **246c**	1.358(4)	1.355(5)	1.420(7)	1.407(4)	1.423(4)	1.356(4)	124.5(3)	114.1(3)	121.4(3)	61.5(2)	57.0(2)	329

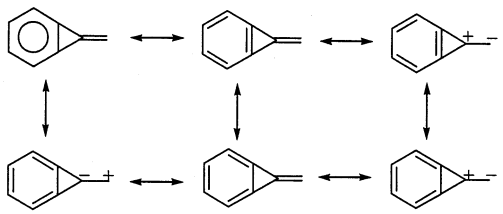


the cyclopropareneyl moiety, e.g., see entries 47/99 vs 53/105 of Table 1, showing that it is ambiphilic.[177,179,180]

The three-membered ring and its adjacent bonds reflect the impact of both the trigonal planar C-1 atom and the charge separation. Like the parent hydrocarbons **2** and **6**, the bridge bond (bond *a*) is shortened compared to benzene but the extent is less. The three-membered ring σ bonds (bonds *e*) are *shortened* compared to the nonalkene parents while angles δ and ϵ are narrowed and widened, respectively, by ca. 2° and 3°. These data are fully compatible with the change at C-1 from tetrahedral to trigonal planar and they fit comfortably with the predicted changes from methylidenecyclopropane to methylidenecyclopropene. The exocyclic olefin length (bond *f*, Table 4) measured for the benzo derivatives **167b**, **243**, and **246** are all *longer* than that computed for parent **139** (1.343, 1.338, and 1.347 vs 1.318 Å) while those for the naphthalene derivatives fall in the range 1.329−1.448 Å. All are compatible with polarization and charge separation within the molecules. Computed structures for the alkylidene derivatives provide the best fit to the experimental values when the HF/6-31G(d,p) basis set is employed; calculations at the MP2/6-31G(d,p) level tend to overestimate the bond lengths by ca. 0.02 Å. In like manner, dipoles calculated at the HF/6-31G(d,p) level tend to be higher than those measured whereas for polar dyes incorporating the cyclopropareneyl moiety (entries 57−61, Table 1) calculations at the HF/STO-3G//HF/6-31G and HF/6-31G levels underestimate the measured values.[180] However, the relative orders are not changed.

The alkylidenecycloproparenes have been subjected to detailed theoretical scrutiny[179] not least because of the incorporation into **139** of all the features of a

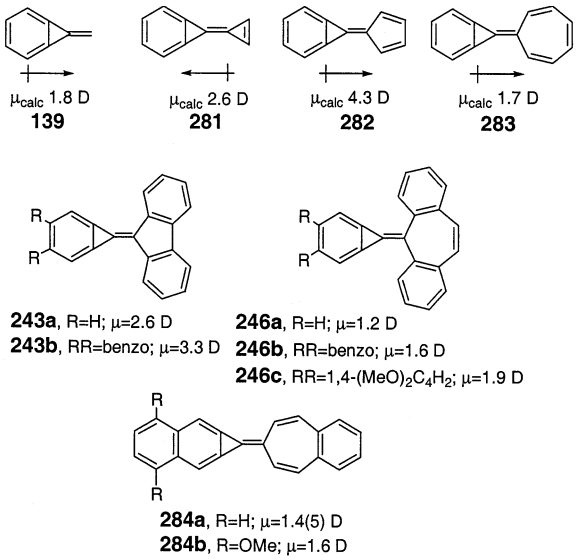
Scheme 66



139

methylidenecyclopropareneyl, a novel fused triafulvene and a trimethylidenecyclopropane (Scheme 66). Fusion of a second conjugated ring, as required for a fulvalene, provides for polar hydrocarbons. However, the calculations show that only the as yet unknown cyclopropenylidene derivative **281** has its dipole (μ 2.6 D) directed *toward* the cyclopropareneyl; the only reported derivatives of this ring system[185] are the symmetrical **175** and **176**. The unknown parent cyclopentadienylidene and cyclopheptatrienylidene derivatives **282** and **283** are predicted polar (μ 4.3 and 1.7 D, respectively) but with the dipole directed away from the cyclopropareneyl. As shown in Chart 4, the known derivatives of **282** and **283**, viz. **243a/b**, and **246a−c** and **284a/b**, are polar (see also Table 1). The expectation, calculation, and observation of the polar cyclopentadienylidene electron sink in **282** and its derivatives **243** are unexceptional. The prediction of a cyclopropenyl cation in **281** is as yet untested though not surprising, but the calculation of a dipole directed toward the traditional electron donating cycloheptatrienylidene moiety as in **283** (to liberate an 8π7C antiaromatic cycloheptatrienyl anion) is unexpected.[179] In light of this, the polarity of **246a**[179] and, more recently, its naphtho homologues **246b** and naphtho-diether **246c** as well as **284a/b**

Chart 4



have been recorded.[165] All these cycloheptatrienylidene derivatives have a permanent dipole and the fact that the diethers are *more* polar than their non-ether counterparts serves to confirm that electron donation is *from* the cyclopropparene *to* the cycloheptatrienylidene moiety. The single-crystal structure of suberone derivative **246a** has been reported[179] and that of its 3,6-dimethoxynaphtho analogue **246c** more recently obtained.[329] The structural data appear in Table 4, but it is the molecular shape that commands greatest attention since the molecules are nonplanar. The (remote) double bond of each seven-membered ring is bent out of the plane holding the cyclopropparene as shown in Figure 5. In hydrocarbon **246a** this

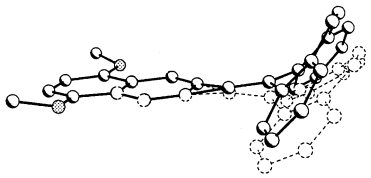


Figure 5. Superimposed partial X-ray structures of cycloheptatrienylidene derivatives **246a** and **246c** showing the ca. 28° and 45° out-of-plane twisting of the seven-membered rings. Data taken from ref 329.

is ca. 28° and in the more polar **246c** ca. 45°. Although steric congestion between the *ortho* hydrogens of the suberone-derived moiety and the fused cyclopropene ring is possible, the observed bending also provides a resistance to any possible antiaromatic character. The fact that the bending is greater in the more polar diether adds further credence to this. In contrast, the fluorenylidene derivatives **243** are essentially planar throughout.[179]

A similar structural feature is recorded for the anthrylidene, acridinylidene, and xanthylidene analogues **285a**−**d**.[180] Here, it is the dimethylanthrylidene **285a** that is nonplanar with the $>CMe_2$ moiety bent significantly out of the plane containing the cyclohexadienylidene unit (Figure 6, upper). However, with an auxochrome present and extended conjugation evident, **285b** and **285d** have X-ray structures

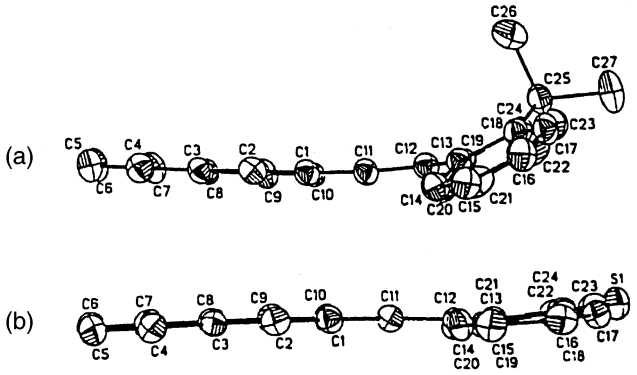
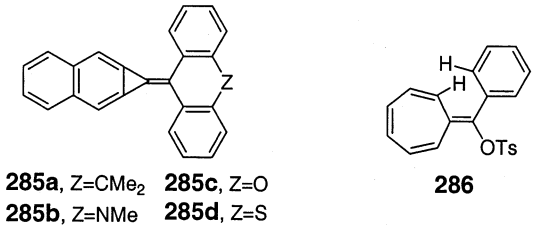


Figure 6. Side view of the X-ray structures of (a) **285a** and (b) **285d** showing the bending of the molecules. Reprinted with permission from ref 180. Copyright 1998 American Chemical Society.

that show near planarity (Figure 6, lower); the structures of the compounds were also computed at the HF/6-31G* level.[180]



Polarity within the wide range of known aryl and diarylmethylidenecyclopropparenes is well established as shown by the measured dipole moments recorded in Tables 1 and 2. Ambiphilicity is evident from the magnitude of the polarity in the archetypical amino acceptors and nitro donors. For example, entries 47 and 99, and 53 and 105 of Table 1 illustrate a diminution of polarity in diether−diamine compared to the non-ether (2.3 vs 3.0 D) but an enhancement in the corresponding dinitro−diether (4.7 vs 4.3 D) as the functionalities oppose and reinforce one another, respectively. Furthermore, the introduction of carbon−carbon double bond spacer groups (see entries 66−74 of Table 1) does not diminish the magnitude of the dipole.[165] Correlations between substituent Hammett σ_p^+ values and the magnitude of the dipole have been made.[165] For mesomerism to be effective good overlap between the π orbitals of the cyclopropparene and those of the pendant arm is needed. In the cyclopropparenefulvene series the conjugating substituent at the exocyclic center is held essential planar when its partner is hydrogen. The (dimethylaminophenyl)methylidene ($Me_2NC_6H_4CH=$) and the 2-thienylmethylidene derivatives have the attached 6π6C and 6π4CS rings a mere 5° out of plane as illustrated for the latter (Figure 7, upper).[164] With the diphenyl-[160] and bis(dimethylaminophenyl)[164] analogues a propeller-shape is adopted about the exocyclic double bond with the aryl substituent rings twisted between 27° and 35° out of plane. This is shown for the diphenyl derivative in the lower part of Figure 7. In the hepta- or pentafulvene series[331−334] diarylmethylidene ($Ar_2C=$) derivatives have the C-8 (or C-6) aromatic rings twisted out of the plane of

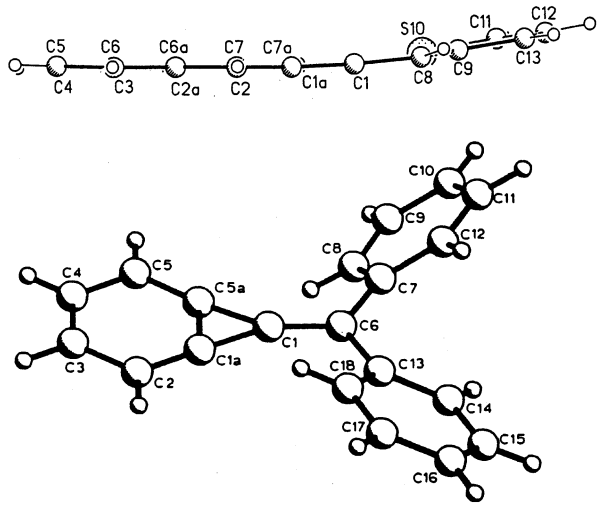


Figure 7. Perspective structural views of 2′-thienyl- (upper) and 1,1-diphenyl- (lower) methylidenecyclopropare-nes. Upper panel reproduced by permission of the Royal Society of Chemistry from ref 164 (Copyright 1995) and lower from ref 160 (Copyright 1986 American Chemical Society).

the seven- (or five)-membered ring by angles in the range 37−45°. For example, the steric interference between the proximal hydrogens of enol tosylate **286** forces a twist of 44.8° in the solid state.[335] The twist angles recorded for the diarylmethylidenecyclopro-parenes are, in fact, more akin to those recorded for various (*E*)-stilbenes[336,337] and nicely consistent with the added spatial freedom available to the exocyclic substituents compared with their heptafulvene ana-logues. After all, the molecules can justifiable be viewed as stable derivatives of a 2,7-didehydrocyclo-heptatrienylidene! With markedly reduced twist angles mesomerism can operate without any need to invoke polarization of the exocyclic double bond as is clearly necessary for the heptafulvalene ana-logues.[331,338]

Semiempirical molecular orbital calculations lead to inaccurate cycloproparene geometries especially in the length of the fusion bond.[4,10] However, there is no such impediment to obtaining a reliable estimate of the heat of formation and strain energy of a given compound. Table 5 provides such data for the es-sential cycloproparenes of which only the strain energies of **2** and **6** have been measured experimen-tally;[24] all other data are from calculation. As can be seen, the computed strain energies of the simple cycloproparenes fall within the range 68−71 kcal mol^{-1}. This compares very favorably with the experi-mental values of 68 and 67.8 kcal mol^{-1} for **2** and **6**, respectively, obtained from Ag(I)-catalyzed metha-nolysis reactions.[24] The values of the strain energies assume that aromatic stabilization energy is the same as that in the parent aromatic compound. Dicyclopropanaphthalene **26** has more bonds to dis-perse strain over than does **2** and so it has about 20 kcal mol^{-1} *less* strain than expected by doubling the value for **2**. In contrast, **287** and **288**, with two three-membered but only the one arene ring, have much closer to double the strain of **2**, and it is the angular isomer that is the more strained of the pair by ca. 7 kcal mol^{-1}. This is mirrored in the data for **5** and **6,** and the benzynes **194** and **195**, where the angular isomers also have the higher strain; the structural expectations[144] of benzyne fit better to the "linear" rather than the "angular" form. It was noted previ-ously[4] that these data suggest the generation and trapping of the dicyclopropabenzenes to be more a function of an appropriate synthetic protocol than the actual stability of the compounds, especially with the knowledge that the benzynes have been generated and trapped at ambient temperature.[195]

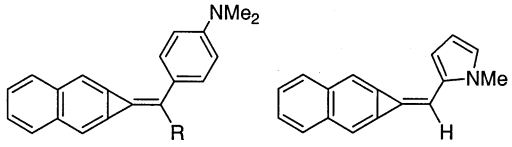
There have been no new photoelectron spectro-scopic data reported for the cycloproparenes and the comments recorded earlier are as valid now as they were then.[4] In similar vein, the electronic absorption spectra of the cycloproparenes (tabulated earlier for the fundamental ring systems[15]) show that the strain imparted to the σ framework does not impact upon the aromatic chromophore. Thus, **2** [λ_{max} (C_6H_{14}) 252 (2.7), 258 (3.0), 264 (3.2) 270 (3.4) and 277 nm (log ϵ 3.3)] and **6** [λ_{max} (C_6H_{14}) 220 nm (log ϵ 4.7)] have absorption maxima that are very similar to the corresponding *o*-dimethyl-substituted aromatic. The fusion of a second small ring effects a bathochromic shift, and for rocketene **28** the shift to longer wave-length is the largest in the series of linearly fused cycloalkacycloproparenes [λ_{max} 284 (∼3.0), 287.5 (∼3.0), and 294 nm (log ϵ 2.8)]. In contrast, that for angular **29** is the smallest among its corresponding analogues [λ_{max} 264 (∼3.1), 279 (∼3.2), and 276.5 nm (log ϵ ∼ 3.2)].[206,342] This is consistent both with the ability of the fused ring to participate in hyperconjugation and with changes in the configurational composition of the excited state.[343]

The UV−vis spectra of the aryl-substituted alky-lidenecycloproparenes show long wavelength absorp-tions in accord with their color, the precise positions

Table 5. Heats of Formation ($\Delta H_f°$) and Strain Energies (SE) of Selected Cycloproparenes (kcal mol^{-1})

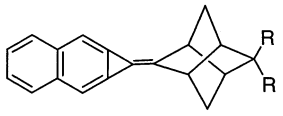
Comp.	**2**	**5**	**6**	**64**	**126**	**26**	**287**	**288**	**289**	**28**	**29**	**195**	**194**
($\Delta H_f°$)	90	109	104	128	126	156	154	160	237, 227	122	123	190	195
Ref.	23	339	339	339	339	340	330	330	330,341	330	330	195	195
SE	68	71	67.8	69	70	120	133	140	217, 207	102	103	170	175
Ref.	24	339	24	339	339	340	330	330	330,341	330	330	195	195

of which are solvent dependent. As solvent polarity is increased the absorption maximum shifts to *shorter* wavelength by up to 7 nm. This move (negative solvatochromy) is in the opposite direction to that expected for a $\pi \rightarrow \pi^*$ transition but it matches well a number of other polar fulvalenes and fulvenes.[344,345] It has been noted earlier that the polar contribution of a dimethylaminophenyl group can be negated simply by protonation, whereupon the absorption maximum reverts to that of the simple phenyl derivative.[177] Despite the color and the availability of dyes containing the cyclopropparene framework,[180] it is the fluorescence characteristics of these compounds that has commanded much attention. Emission spectra for a range of derivatives have been obtained, and the cyclopropparene lumophore assessed.[4,164,191,203,346] Without doubt, the amino auxochrome is the most effective, be it as the dimethylaminophenyl **168e/f** or pyrrolyl **290** derivative. Unfortunately, the latter has limited stability in air.[164] The **168e/f** pair have absolute quantum yields for emission (ϕ) of 0.96 and 0.81, respectively, and significantly more polar excited states.[346] Furthermore, the stationary excitation spectra of **168e** in a range of solvents are independent of the emission wavelength and the same as the absorption spectra.[347] The quantum yield lies between 0.9 and 1.0 and the fluorescence maximum varies in the range 474−543 nm in MeCN. Most of the alkylidenecyclopropparenes prepared display fluorescence characteristics, but it is these specific compounds that are the most active. The recently prepared derivatives **291** from stellanone and stellanedione (see entries 64 and 65, Table 1) also show good fluorescence properties, but unfortunately the molecules are photolabile.[203]



168e, R=H
168f, R=*p*-$Me_2NC_6H_4$

290



291, R=H or RR=O

The infrared spectra of the cyclopropparenes are unexceptional but fully compatible with the symmetry of the molecules. A combination aromatic double bond stretch with a three-membered ring skeletal vibration is responsible for a characteristic absorption at ca. 1660 cm^{-1} as demonstrated by peaks at 1666, 1673, 1678, and 1687 cm^{-1} for **2**, **6**, **64**, and **5**, respectively. For the alkylidene derivatives characteristic stretching frequencies are recorded in the ranges 1510−1550 and 1760−1790 cm^{-1} that mirror the 1510−1550 and 1810−1880 cm^{-1} of the alkylidenecyclopropenes (1519 and 1770 cm^{-1} for methylidenecyclopropene itself[348−350]). The ca. 1770 cm^{-1} stretch is weak and varies in intensity with the molecular polarity, the more polar compounds exhibiting a weakened stretch that appears at lower wavenumber. In fact, the stretches for the mesomerically conjugated and fluorescent dimethylamino derivatives **168e/f** (ca. 1750 cm^{-1}) are markedly increased in intensity upon quaternization[164,177] and their positions shifted to ca. 1775 cm^{-1}.

In the NMR domain, the cyclopropparenes exhibit a typical aromatic ring current with the arene protons resonating in the normal range. Thus, for **2** an AA′BB′ pattern is recorded at 7.149 and 7.189 ppm for H2/5 and H3/4, respectively. The methylene group appears at 3.11 ppm and the range for the family of compounds is 3.0−3.6 ppm. In cyclopropa[*b*]naphthalene (**6**) H2/7 appear as a singlet at δ 7.57, and H3−H6 as an AA′BB′ system in the ranges δ 7.43−7.46 and 7.86−7.89. The alkylidene derivatives are similar save for the absence of the H1 protons. The hydrogens located adjacent to the three-membered ring fusion sites appear as a sharp singlet for the symmetrical derivatives but as *para*-coupled doublets (J ca. 1.5 Hz) when the olefin is monosubstituted. The value of J_{para} is inconsistent with unstrained aromatics as the cyclopropparenes give magnitudes of J_{meta} (0.3−0.7 Hz) and J_{para} (1.5−1.7 Hz) that are a reversal of the norm. H2/H5(7) may or may not be discernible from overlapping aromatic proton signals of the substituent moieties. When symmetrical, the low field arm of the H3−H6 AA′BB′ pattern is usually visible and, depending upon the extent of asymmetry, may remain so in a monosubstituted alkene.

It is the ^{13}C NMR data that provide the most useful and diagnostic spectral information. All cyclopropparenes have the resonances of the carbon atoms adjacent to the three-membered ring fusion (C2/5 in **2** and C2/7 in **6**, and their respective derivatives) shielded in comparison to the parent arene and resonating in the range 95−115 ppm. The appearance of signals in this range may be taken as diagnostic of the family and used as confirmation for the presence of the ring system. For **2** and **6** these carbons appear at 114.7 and 112.3 ppm thereby displaying shielding of 13.8 and 15.7 ppm compared with benzene and naphthalene, respectively. The impositions of additional strain as, e.g., in **28** and **29**, has markedly less impact as the C2 resonances are only marginally further shifted appearing at 111.0 and 112.4 ppm. The influence of strain is also evident in the $^1J_{C-H}$ couplings of C2−H with a value of ca. 170 Hz the norm. There is a gradation in magnitude of $^1J_{C-H}$ in moving from cyclopenta- (indane) to cyclobuta- to cyclopropabenzene (155.5, 162, and 168.5 Hz). The one-bond C−H couplings at the benzylic center (C-1 in **2**) for the same three compounds follow a similar pattern but over a much wider range, viz. 127, 138, and 170 Hz. With the advent of 2D NMR spectroscopy as a routine tool many of the earlier assignments have been confirmed. The cyclopropanaphtho- and anthraquinones **191** and **218** provide data that fit nicely with the cyclopropparenes. Both compounds have H1 at 3.36 ppm and C2/7 is at 112.8 for **191** and 113.2 ppm for **218**.

In the alkylidenecyclopropparenes, the impact of mesomerism has been confirmed from correlation of the carbon chemical shifts of the cyclopropparenyl unit with the Hammett σ_p^+ constant of the *para*-substituent of a pendant aryl group.[351] The systematic influence of the substituents on the chemical shift unquestionably established mesomeric resonance contributions but the range of examples initially studied was limited. A far more comprehensive study embodying some 60 compounds,[165] has provided definitive evidence to show the cyclopropparene frame as an *electron donor* that gives a linear correlation of each carbon from C1 to C8 of a methylidenecyclopropa[*b*]naphthalene (**168**) with σ_p^+ of the remote substituent. This is illustrated here simply for phenylmethylidene derivatives of Figure 8, but equally

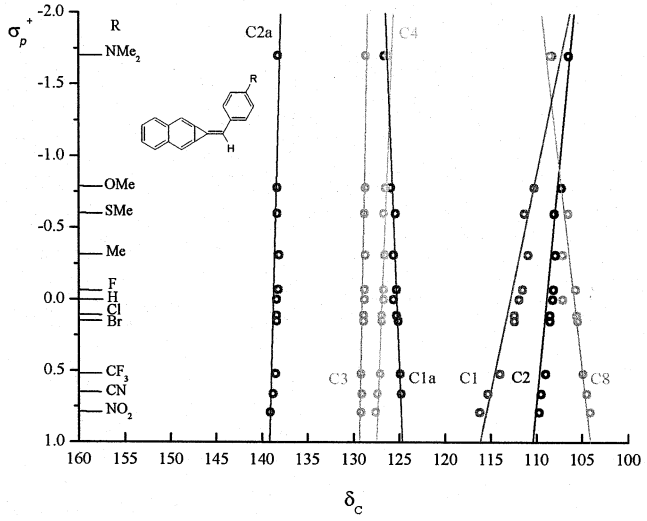


Figure 8. ^{13}C NMR chemical shift vs σ_p^+ correlations for 1-arylmethylidenecyclopropa[*b*]naphthalenes (**167**). Unpublished data from ref 165.

good correlations apply to diaryl and arylphenyl analogues.[165] The carbons of the exocyclic bond are usually discernible and their relative positions, like those for all carbons of the molecules involved, have been established from 2D NMR experiments. In general, C1 appears in the range 105−120, the exocyclic center C6 (or C8) 104−112, C2/5 100−112, and C3/4 132−136 ppm. The incorporation of methoxy functions into cyclopropanaphthalene is not untoward and normal aromatic substituent effects operate for the 3,6-dimethoxyether and its range of exocyclic alkenes.[352]

The quinones **191** and **218** have been subjected to cyclic voltammetry, and this shows them to behave in a manner very similar to their parents. Thus, **191** is only 0.5 V more difficult to reduce than 1,4-naphthoquinone,[64] while **218** give a cyclic voltammogram that is essentially that same as that from 9,10-anthraquinone under the same conditions.[214] Radical anions **250** and radical cations **251** have been generated from the diphenylmethylidene compounds **167b** and **168b** in electrochemical and spectroelectrochemical studies that show the oxidation and reduction steps to be reversible.[287,288] Each compound affords a stable radical anion **250** [λ_{max} 519 (ex-**167b**) and 587 nm (ex-**168b**)] and a quasi-stable radical cation **251**. The half-wave oxidation potentials ($E_{1/2}^{\bullet+}$) for **167b** and **168b** (0.68 and 0.81 eV, respectively) are in reverse order to the norm whereby the more delocalized system is the more easily oxidized. Photoelectron spectra reveal that the observed differences in the $E_{1/2}^{\bullet+}$ values have no analogy in the gas phase where the first ionization potential of the two compounds is essential the same.[353]

Molecular ions are usually observed in the electron impact mass spectra of the cyclopropparenes[354] and fragmentation by loss of radical from C-1 to give a cyclopropabenzenyl cation is the norm. The alkylidene derivatives invariably show the molecular ion as the base peak of a simple spectrum. Use of softer ionization techniques can be employed and electrospray spectra are often easier to obtain that those from APCI.

VI. Cyclopropparenyl Cations, Anions, Radicals, and Carbenes

The existence of the cyclopropparenyl cation was confirmed from the 1974 isolation of **177** as its hexachloroantimonate from reaction of **43** with antimony pentachloride (Scheme 31).[192] The formation of cations upon ionization of the C-1 halides is well recognized and they have been characterized by ^{1}H and ^{13}C NMR spectroscopy.[88,193] No further discussion of these species is justified here as there have been few recent studies save for the discussion of a reversed Mills−Nixon effect in the cations.[355]

Use of the cyclopropparenyl anion in synthesis has played a major role in the development of cyclopropparene chemistry and, as such, the use of the anions in synthesis has been integrated throughout this discussion. To date, attempts to characterize the anion spectroscopically have failed[356] and the derived radical anion is too reactive for detection from conventional electron-transfer techniques; dimerization into the tetracene manifold takes place rapidly.[268] Suffice it here to reiterate that characterization of **159** in the gas phase has been achieved.[219] As noted earlier, these studies have allowed for the thermodynamic stability of anion **159** to be assessed. The measured acidity of cyclopropabenzene (**2**) is $\Delta H^\circ_{acid} = 386 \pm 3$ kcal mol^{-1}. This value is some 34.5 kcal mol^{-1} *more acidic* than that for loss of a C-3 proton from cyclopropene and 4 ± 3 kcal mol^{-1} *less acidic* than toluene; the experimental findings were satisfactorily reproduced by ab initio calculations at the MP2(fc)/6-31+G(d)//HF/6-31+g(d) and MP2(fc)/6-31+G(d) levels of theory.[219] The increased acidity of **2** compared with cyclopropene is rationalized by interplay between the ability of the aromatic ring to alleviate unfavorable interaction within a 4π electron three-membered ring and pyramidalization at C-1 that minimizes interaction of the anion with the aromatic sextet. The geometry of **159** has been computed at the MP2(fc)/6-31+G(d) level and is as shown in Figure 9. The pyramidalization about C-1 (56.5°) is *less* than for the computed structure of the cyclopropenyl anion and this is attributed to a greater facility for delocalization of charge in **159**. The changes in bond lengths about the three-membered ring are significant and parallel the changes in going

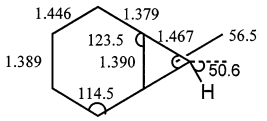


Figure 9. Calculated bond lengths (Å) and angles (°) for anion **159**. Data taken from ref 219.

from **2** to trigonal planar methylidene-**167** insofar as the lateral σ bond is shortened and the bridge bond lengthened; this fits with enhanced *s*-character at C-1.

Whereas the existence of diradical-carbene from homolytic cleavage of the cycloproparene σ bond of **2** and **6** is established,[267,269] there are no known reports of a cycloproparenyl radical at C-1 other than by calculation.[357] The deployment of *gem*-dichlorocyclopropарene **43** as a potential radical source failed.[358] It remains to be seen whether the cycloproparenes can be transformed, e.g., via anion **159** or **160**, into an appropriate radical precursor. Much care will be needed as the studies in these laboratories have demonstrated many difficulties with such simple transformations.[161,162,175,187] Attempts to form radicals in the alkylidenecyclopropарene series also have not been successful.[226]

The only evidence for the existence of a cyclopropарenylidene, a carbene at the C1 center of a cycloproaprene, stems from the observation of coupled products **175** and **176** from the *gem*-dichlorocyclopropabenzenes derivatives **43** and **174**, respectively.[185] The fact that each product is formed after low-temperature lithium−halogen exchange provides a clear indication that carbenoid is involved but the existence of an analogue in the naphthalene series in more speculative since the products of reaction could not be characterized.[191] At the present time, no other C1-substituted cycloproparene suitably for carbene generation is available. Indeed, much remains to be done in studying the chemistry of functionalized cycloproparenes.

VII. Acknowledgment

I would like to thank my co-workers whose names appear in the citations. Without them, little, if any, of the work from the Wellington laboratory would have reached fruition. They have made life in the strain game that much more enjoyable! Financial support from Victoria University is gratefully acknowledged.

VIII. Note Added in Proof

The X-ray structural details of encapsulated benzocyclopropenone **144** (Figure 1, section IID) have been made available. Warmuth and his colleagues[359] provide the critical confirmation that encapsulated **144** is present and essentially planar inside its host. The size and nature of the host have precluded highly accurate structural data; *all* the six-membered ring internal bond angles are 120(5)° bonds and the bond lengths vary from 1.39(9)−1.40(8) Å as shown in Figure 10. The uncertainties associated with these data cover the range of bond length and angle

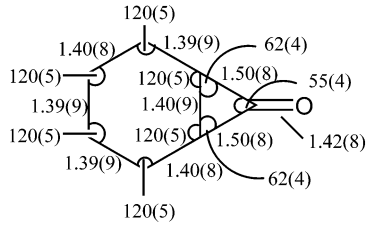


Figure 10. Bond lengths (Å) and angles (°) of encapculated **144**. Data taken from ref 359.

deviations found in the cycloproparenes (Tables III and IV, section V).

Tokitoh's group at Kyoto have reported[360] the synthesis of **292**, the first germacyclopropabenzene that carries the very bulky Tbt and Dip substituents (defined in Scheme 65, section IV). The molecule, the congener of silane **274**, was obtained in 40% yield using a route paralleling that for **274**, and it has been fully characterized by ^{1}H, ^{13}C, FAB-MS, and X-ray structural analysis. The structural details (Figure 11)

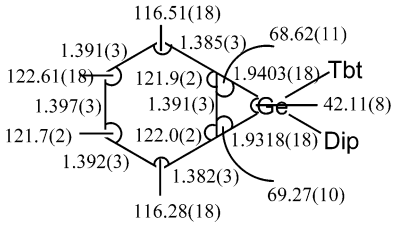


Figure 11. Bond lengths (Å) and angles (°) of **292**. Data taken from ref 360.

show good agreement with theoretical calculations and have the germacyclopropabenzene moiety planar. *The six-membered ring bonds are unperturbed* and fall within the normal range (1.39−1.40 Å) for aromatics. The equivalent angles C1a−C2−C3 and C4−C5−C5a are narrowed to 116.4°, a value surprisingly slightly narrower than the 117.3° recorded for **274**. This could be an experimental artifact as the general conclusion is that in the series **2**, **274**, and **292** the larger heteroatom will cause less distortion of the fused-ring structure. This was borne out by calculations that included the unknown parent tin and lead derivatives. The remaining benzenoid angles of **292** are close to 122°. The Ge−C1a(5a) lengths are ∼1.935 Å and the C1a−Ge−C5a angle is narrowed to 42.11(8)°, while the Ge−C1a(5a)−C5a(1a) angles are widened to ∼69°; these compare with 52.8° and 63.6°, respectively, of **2** (Table 3, section V).

IX. References

(1) Anet, R.; Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 525.
(2) Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625.
(3) Perkin, W. H. *J. Chem. Soc.* **1888**, 1.
(4) Halton, B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1995; Vol. 2.
(5) De, S. C.; Dutt, D. N. *J. Indian Chem. Soc.* **1930**, *7*, 537.
(6) Halton, B.; Harrison, S. A. R.; Spangler, C. W. *Aust. J. Chem.* **1975**, *28*, 681.
(7) Mustafa, A.; Kamel, M. *J. Am. Chem. Soc.* **1953**, *75*, 2939.
(8) Jones, G. W.; Kerur, D. R.; T., Y.; Shechter, H.; Woolhouse, A. D.; Halton, B. *J. Org. Chem.* **1974**, *39*, 492.
(9) Pinkus, A. G.; Tsuji, J. *J. Org. Chem.* **1974**, *39*, 497.
(10) Halton, B. *Chem. Rev.* **1989**, *89*, 1161.
(11) Halton, B. *Chem. Rev.* **1973**, *73*, 113.
(12) Ullman, E. F.; Buncel, E. *J. Am. Chem. Soc.* **1963**, *85*, 2106.

(13) Roberts, J. D.; Streitweiser, A.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579.
(14) Battiste, M. A.; Halton, B. *J. Chem. Soc., Chem. Commun.* **1968**, 1368.
(15) Halton, B. *Ind. Eng. Chem., Prod. Res. Dev.* **1980**, *19*, 349.
(16) Halton, B.; Stang, P. J. *Acc. Chem. Res.* **1987**, *20*, 443.
(17) Halton, B.; Stang, P. J. *Synlett* **1997**, 145.
(18) Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.
(19) Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305.
(20) Müller, P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 3.
(21) Müller, P. In *Carbocyclic Three-Membered Ring Compounds*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Vol. E 17 d.
(22) Wege, D. *Eur. J. Org. Chem.* **2001**, 849.
(23) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1986**, *108*, 3241.
(24) Billups, W. E.; Chow, W. Y.; Leavell, K. H.; Lewis, E. S.; Margrave, J. L.; Sass, R. L.; Shieh, J. J.; Werness, P. G.; Wood, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 7878.
(25) Buchholz, L., University of Heidelberg, personal communication, October, 1989.
(26) Fehr, O. C.; Grapenthin, O.; Kilian, J.; Kirmse, W.; Steenken, S. *Tetrahedron Lett.* **1995**, *36*, 5887.
(27) Baum, G.; Bernard, R.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 5307.
(28) Staab, H. A.; Ipaktschi, J. *Chem. Ber.* **1968**, *101*, 1457.
(29) Schrader, L. *Tetrahedron* **1973**, *29*, 1833.
(30) Hirakawa, K.; Minami, Y.; Hayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 577.
(31) Hirakawa, K.; Toki, T.; Yamazaki, K.; Nakazawa, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1944.
(32) Burgert, W.; Grosse, M.; Rewicki, D. *Chem. Ber.* **1982**, *115*, 309.
(33) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311.
(34) Bambal, R.; Fritz, H.; Rihs, G.; Tschamber, T.; Streith, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 668.
(35) Huben, K.; Kuberski, S.; Frankowski, A.; Gebicki, J.; Streith, J. *J. Chem. Soc., Chem. Commun.* **1995**, 315.
(36) Buckland, S. J.; Halton, B.; Stanovnik, B. *Tetrahedron Lett.* **1986**, *27*, 1309.
(37) Payne, A. D.; Wege, D. *Perkin Trans. 1* **2001**, 1579.
(38) Dürr, H.; Schrader, L. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 446.
(39) Dürr, H.; Schrader, L. *Chem. Ber.* **1970**, *103*, 1334.
(40) Dürr, H.; Schrader, L.; Seidl, H. *Chem. Ber.* **1971**, *104*, 391.
(41) Dürr, H.; Schmitz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 647.
(42) Braun, S.; Sturm, V.; Runzheimer, K.-O. *Chem. Ber.* **1988**, *121*, 1017.
(43) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. *Org. Synth.* **1976**, *55*, 12.
(44) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. *J. Chem. Soc., Chem. Commun.* **1971**, 1461.
(45) Billups, W. E.; Chow, W. Y. *J. Am. Chem. Soc.* **1973**, *95*, 4099.
(46) Halton, B.; Diggins, M. D.; Kay, A. J. *J. Org. Chem.* **1992**, *57*, 4080.
(47) Prestien, J.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 276.
(48) Banwell, M. G.; Blattner, R.; Browne, A. R.; Craig, J. T.; Halton, B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2165.
(49) Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. M. *J. Org. Chem.* **1980**, *45*, 4183.
(50) Neidlein, R.; Poignée, V. *Chem. Ber.* **1988**, *121*, 1199.
(51) Halton, B.; Randall, C. J.; Gainsford, G. J.; Robinson, W. T. *Aust. J. Chem.* **1987**, *40*, 475.
(52) Halton, B.; Randall, C. J. *Tetrahedron Lett.* **1982**, *23*, 5591.
(53) Garratt, P. J.; Koller, W. *Tetrahedron Lett.* **1976**, 4177.
(54) Billups, W. E.; Chamberlain, W. T.; Asim, M. Y. *Tetrahedron Lett.* **1977**, 571.
(55) Kumar, A.; Tayal, S. R.; Devaprabhakara, D. *Tetrahedron Lett.* **1976**, 863.
(56) Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 736.
(57) Halton, B.; Boese, R.; Bläser, D.; Lu, Q. *Aust. J. Chem.* **1991**, *44*, 265.
(58) Vogel, E.; Sombroek, J. *Tetrahedron Lett.* **1974**, 1627.
(59) Banwell, M. G.; Halton, B.; Hambly, T. W.; Ireland, N. K.; Papamihail, C.; Russell, S. G. G.; Snow, M. R. *J. Chem. Soc., Perkin Trans 1* **1992**, 715.
(60) Davalian, D.; Garratt, P. J. *J. Am. Chem. Soc.* **1975**, *97*, 6883.
(61) Davalian, D.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 980.
(62) Davalian, D.; Garratt, P. J. *Tetrahedron Lett.* **1976**, 2815.
(63) Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.
(64) Halton, B.; Kay, A. J.; Zhi-mei, Z.; Boese, R.; Haumann, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1445.
(65) Halton, B.; Kay, A. J.; Zha, Z. M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2239.
(66) Halton, B.; Lovett, E. G. *Struct. Chem.* **1991**, *2*, 147.
(67) Halton, B.; Bridle, J. H.; Lovett, E. G. *Tetrahedron Lett.* **1990**, *31*, 1313.
(68) Anthony, I. J.; Kang, Y. B.; Wege, D. *Tetrahedron Lett.* **1990**, *31*, 1315.
(69) Collis, G. E.; Jayatilaka, D.; Wege, D. *Aust. J. Chem.* **1997**, *50*, 505.
(70) Law, D. F. C.; Tobey, S. W. *J. Am. Chem. Soc.* **1968**, *90*, 2376.
(71) Apeloig, Y.; Arad, D.; Kapon, M.; Wallerstein, M. *Tetrahedron Lett.* **1987**, *28*, 5917.
(72) Müller, P.; Bernardinelli, G.; Rodriguez, D.; Pfyffer, J.; Schaller, J.-P. *Helv. Chim. Acta* **1988**, *71*, 544.
(73) Müller, P.; Bernardinelli, G.; Rodrugez, D.; Pfyffer, J.; Schaller, J.-C. *Chimia* **1987**, *41*, 244.
(74) Billups, W. E.; Lin, L.-J.; Arney, B. E.; Rodin, W. A.; Casserly, E. W. *Tetrahedron Lett.* **1984**, *25*, 3935.
(75) Vogel, E.; Korte, S.; Grimme, W.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 289.
(76) Glück, C.; Poignée, V.; Schwager, H. *Synthesis* **1987**, 260.
(77) Halton, B.; Milsom, P. J.; Woolhouse, A. D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 731.
(78) Halton, B.; Milsom, P. J. *J. Chem. Soc., Chem. Commun.* **1971**, 814.
(79) Browne, A. R.; Halton, B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1177−1182.
(80) Browne, A. R.; Halton, B. *J. Chem. Soc., Chem. Commun.* **1972**, 1341.
(81) Müller, P.; Thi, H. C. N. *Isr. J. Chem.* **1981**, *21*, 135.
(82) Müller, P.; Nguyen-Thi, H.-C. *Tetrahedron Lett.* **1980**, *21*, 2145.
(83) Müller, P.; Rey, M. *Helv. Chim. Acta* **1981**, *64*, 354.
(84) Müller, P.; Rey, M. *Helv. Chim. Acta* **1982**, *65*, 1157.
(85) Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1983**, *66*, 2540.
(86) Müller, P.; Miao, Z. *Helv. Chim. Acta* **1994**, *77*, 1826.
(87) Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1986**, *69*, 1546.
(88) Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1986**, *69*, 1546.
(89) Müller, P.; Nguyen-Thi, H.-C. *Helv. Chim. Acta* **1984**, *67*, 467.
(90) Halton, B.; Officer, D. L. *Aust. J. Chem.* **1983**, *36*, 1291.
(91) Müller, P.; Thi, H. C. N. *Chimia* **1985**, *39*, 362.
(92) Anthony, I. J.; Wege, D. *Aust. J. Chem.* **1996**, *49*, 1263.
(93) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.
(94) Dent, B. R.; Halton, B.; Smith, A. M. F. *Aust. J. Chem.* **1986**, *39*, 1621.
(95) Müller, P.; Schaller, J.-P. *Helv. Chim. Acta* **1990**, *73*, 1228.
(96) Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1985**, *68*, 975.
(97) Billups, W. E.; Casserly, E. W.; Arney, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 440.
(98) Billups, W. E.; Arney, B. E.; Lin, L.-J. *J. Org. Chem.* **1984**, *49*, 3436.
(99) Billups, W. E.; Haley, M. M.; Claussen, R. C.; Rodin, W. A. *J. Am. Chem. Soc.* **1991**, *113*, 4331.
(100) Billups, W. E.; Luo, W.; Harmon, D.; McCord, D.; Wagner, R. *Tetrahedron Lett.* **1997**, *38*, 4533.
(101) Billups, W. E.; Luo, W.; McCord, D.; Wagner, R. *Pure Appl. Chem.* **1996**, *68*, 275.
(102) Billups, W. E.; McCord, D. J.; Maughon, B. R. *J. Am. Chem. Soc.* **1994**, *116*, 8831.
(103) Billups, W. E.; Luo, W.; Wagner, R.; Hopf, H.; König, B.; Psiorz, M. *Tetrahedron* **1999**, *55*, 10893.
(104) Cooney, M. J.; Halton, B. *Aust. J. Chem.* **1996**, *49*, 533.
(105) Banwell, M. G.; Halton, B. *Tetrahedron Lett.* **1979**, 3191.
(106) Sims, C. G.; Wege, D. *Aust. J. Chem.* **1995**, *48*, 469.
(107) Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84.
(108) Garratt, P. J.; Payne, D.; Tsotinis, A. *Pure Appl. Chem.* **1990**, *62*, 525.
(109) Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145.
(110) Müller, P.; Schaller, J.-P. *Chimia* **1986**, *40*, 430.
(111) Müller, P.; Schaller, J.-P. *Helv. Chim. Acta* **1989**, *72*, 1608.
(112) Müller, P.; Schaller, J.-P. *Tetrahedron Lett.* **1989**, *30*, 1507.
(113) Watabe, T.; Okada, K.; Oda, M. *J. Org. Chem.* **1988**, *53*, 216.
(114) Halton, B.; Dent, B. R.; Bohm, S.; Officer, D. L.; Schmickler, H.; Schophoff, F.; Vogel, E. *J. Am. Chem. Soc.* **1985**, *107*, 7175.
(115) Dent, B. R.; Halton, B. *Aust. J. Chem.* **1987**, *40*, 925.
(116) Dent, B. R.; Halton, B. *Aust. J. Chem.* **1986**, *39*, 1789.
(117) Müller, P.; Thi, H. C. N.; Pfyffer, J. *Helv. Chim. Acta* **1986**, *69*, 855.
(118) Halton, B.; Officer, D. L. *Aust. J. Chem.* **1983**, *36*, 1167.
(119) Brinker, U. H.; Wüster, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 577.
(120) Galloway, N.; Halton, B. *Aust. J. Chem.* **1979**, *32*, 1743.
(121) Galloway, N.; Dent, B. R.; Halton, B. *Aust. J. Chem.* **1983**, *36*, 593.
(122) Tanimoto, S.; Schäfer, R.; Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 613.
(123) Vogel, E.; Püttmann, W.; Duchatsch, W.; Schieb, T.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 720.
(124) Klärner, F.-G.; Dogan, B. M. J.; Weider, R.; Ginsburg, D.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 346.
(125) Batsanov, A. S.; Brooke, G. M.; Drury, C. J.; Howard, J. A. K.; Lehmann, C. W. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1991.

(126) Suzzarini, L.; Lin, J.; Wang, Z. Y. *Tetrahedron Lett.* **1998**, *39*, 1695.
(127) Parham, W. E.; Jones, L. D.; Sayed, Y. A. *J. Org. Chem.* **1976**, *41*, 1184.
(128) Radlick, P.; Crawford, H. T. *J. Chem. Soc., Chem. Commun.* **1974**, 127.
(129) Chuah, T. S.; Craig, J. T.; Halton, B.; Harrison, S. A. R.; Officer, D. L. *Aust. J. Chem.* **1977**, *30*, 1769.
(130) Brewer, P. D.; Tagat, J.; Hergruetner, C. A.; Helquist, P. *Tetrahedron Lett.* **1977**, 4573.
(131) McNichols, A. T.; Stang, P. J. *Synlett* **1992**, 971.
(132) Saward, C. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1975**, 4539.
(133) Halton, B.; Dixon, G. M. *Org. Lett.*, **2002**, *4*, 4563.
(134) Fields, E. K.; Meyerson, S. *J. Chem. Soc., Chem. Commun.* **1965**, 474.
(135) Brown, R. F. C.; Gardner, D. V.; McOmie, J. F. W.; Solly, R. K. *Aust. J. Chem.* **1967**, *20*, 139.
(136) Brown, R. F. C.; Solly, R. K. *Aust. J. Chem.* **1966**, *19*, 1045.
(137) Adamson, J. B.; Forster, D. L.; Gilchrist, T. L.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1969**, 221.
(138) Adamson, J.; Forster, D. L.; Gilchrist, T. L.; Rees, C. W. *J. Chem. Soc., C* **1971**, 981.
(139) Ao, M. S.; Burgess, E. M.; Schauer, A.; Taylor, E. A. *J. Chem. Soc., Chem. Commun.* **1969**, 220.
(140) Simon, J. G. G.; Münzel, N.; Schweig, A. *Chem. Phys. Lett.* **1990**, *170*, 187.
(141) Simon, J. G. G.; Schweig, A.; Xie, Y.; Schaefer, H. F. I. *Chem. Phys. Lett.* **1992**, *200*, 631.
(142) Simon, J. G. G.; Schweig, A. *Chem. Phys. Lett.* **1993**, *201*, 377.
(143) Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1347.
(144) Warmuth, R. *Eur. J. Org. Chem.* **2001**, 423.
(145) Radziszewski, J. G.; Hess, B. A.; Zahradnik, R. *J. Am. Chem. Soc.* **1992**, *114*, 52; Radziszewski, J. G.; Waluk, J.; Kaszynski, P.; Spanget-Larsen, J. *J. Phys. Chem. A* **2002**, *106*, 6730.
(146) Chapman, O. L.; Chang, C.-C.; Kole, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586.
(147) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134.
(148) Sato, T.; Moriyama, M.; Niino, H.; Yabe, A. *J. Chem. Soc., Chem. Commun.* **1999**, 1089.
(149) Sato, T.; Niino, H.; Yabe, A. *J. Phys. Chem.* **2001**, *105*, 7790.
(150) Tomioka, H.; Akuno, A.; Sugiyama, T.; Murata, S. *J. Org. Chem.* **1995**, *60*, 2344.
(151) Murata, S.; Yamamoto, T.; Tomioka, H.; Lee, H.-k.; Kim, H.-R.; Yabe, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1258.
(152) Murata, S.; Yamamoto, T.; Tomioka, H. *J. Am. Chem. Soc.* **1993**, *115*, 4013.
(153) Murata, S.; Kobayashi, J.; Kongau, C.; Miyata, M.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **2000**, *65*, 6082.
(154) Reinecke, M. G.; Chen, L.-J.; Almqvist, A. *J. Chem. Soc., Chem. Commun.* **1980**, 585.
(155) Teles, J. H.; Hess, B. A.; Schaad, L. J. *Chem. Ber.* **1992**, *125*, 423.
(156) Moriyama, M.; Ohana, T.; Yabe, A. *J. Am. Chem. Soc.* **1997**, *119*, 9, 10229.
(157) Moriyama, M.; Ohana, T.; Yabe, A. *Chem Lett.* **1995**, 557−558; Arulmozhiraja, S.; Sato, T.; Yabe, A. *J. Comput. Chem.* **2001**, *22*, 923.
(158) Sato, T.; Arulmozhiraja, S.; Niino, H.; Sasaki, S.; Matsuura, T.; Yabe, A. *J. Am. Chem. Soc.* **2002**, *124*, 4512.
(159) Halton, B.; Randall, C. J.; Stang, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 6108.
(160) Halton, B.; Randall, C. J.; Gainsford, G. J.; Stang, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 5949.
(161) Halton, B.; Jones, C. S.; Northcote, P. T.; Boese, R. *Aust. J. Chem.* **1999**, *52*, 285.
(162) Halton, B.; Jones, C. S. *J. Chem. Soc., Perkin Trans. 2* **1998 (1999)**, 2505 (387).
(163) Cutler, C. A.; Halton, B. *Aust. J. Chem.* **1997**, *50*, 267.
(164) Halton, B.; Cooney, M. J.; Davey, T. W.; Forman, G. S.; Lu, Q.; Boese, R.; Bläser, D.; Maulitz, A. H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2819.
(165) Dixon, G. M., Ph.D. Thesis, Victoria University of Wellington, 2002.
(166) Müller, P.; Bernardinelli, G.; Jacquier, Y. *Helv. Chim. Acta* **1992**, *75*, 1995.
(167) Müller, P.; Bernardinelli, G.; Jacquier, Y.; Ricca, A. *Helv. Chim. Acta* **1989**, *72*, 1618.
(168) Halton, B.; Buckland, S. J.; Lu, Q.; Mei, Q.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 2418.
(169) Lu, Q. Ph.D. Thesis, Victoria University of Wellington, 1989.
(170) Halton, B.; Ward, J. M., unpublished results, 2001.
(171) Halton, B.; Lu, Q.; Stang, P. J. *Aust. J. Chem.* **1990**, *43*, 1277.
(172) Halton, B.; Davey, T. W., unpublished observations, 1993.
(173) Halton, B.; Forman, G. S., unpublished observations, 1994.
(174) McNichols, A. T.; Stang, P. J., unpublished observations.
(175) Jones, C. S. Ph.D. Thesis, Victoria University of Wellington, 2001.
(176) Halton, B.; Jones, C. S., unpublished observations, 1999.
(177) Halton, B.; Lu, Q.; Stang, P. J. *J. Chem. Soc., Chem. Commun.* **1988**, 879.
(178) Stang, P. J.; Song, L.; Lu, Q.; Halton, B. *Organometallics* **1990**, *9*, 2149.
(179) Apeloig, Y.; Boese, R.; Bläser, D.; Halton, B.; Maulitz, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 10147.
(180) Halton, B.; Cooney, M. J.; Boese, R.; Maulitz, A. H. *J. Org. Chem.* **1998**, *63*, 1583.
(181) Fritzche, G.; Gleiter, R.; Irngartinger, H.; Oeser, T. *Eur. J. Chem.* **1999**, 73.
(182) Buckland, S. J.; Halton, B.; Stang, P. J. *Aust. J. Chem.* **1988**, *41*, 845.
(183) Halton, B. *Pure Appl. Chem.* **1990**, *62*, 541.
(184) Halton, B.; Buckland, S. J.; Mei, Q.; Stang, P. J. *Tetrahedron Lett.* **1986**, *27*, 5159.
(185) Neidlein, R.; Poignée, V.; Kramer, W.; Glück, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 731.
(186) McNichols, A. T.; Stang, P. J.; Addington, D. M.; Halton, B. *Tetrahedron Lett.* **1994**, *35*, 437.
(187) Halton, B.; Jones, C. S.; Margetic, D. *Tetrahedron* **2001**, *57*, 3529.
(188) Halton, B.; Jones, C. S.; Parkin, C. T., unpublished observations, 2001.
(189) Bloch, R.; Orvane, P. *Tetrahedron Lett.* **1981**, *22*, 3597.
(190) O'Leary, M. A.; Wege, D. *Tetrahedron Lett.* **1978**, 2811.
(191) Cooney, M. J.; Halton, B., unpublished observations, 1994; Halton, B. The 9th International Symposium on Novel Aromatic Compounds (ISNA-9): Hong Kong, August 1998, Abstract IL03.
(192) Halton, B.; Woolhouse, A. D.; Hugel, H. M.; Kelly, D. P. *J. Chem. Soc., Chem. Commun.* **1974**, 247.
(193) Halton, B.; Hugel, H. M.; Kelly, D. P.; Muller, P.; Burger, U. *J. Chem. Soc., Perkin Trans. 2* **1976**, 258.
(194) Gaber, A. E.-A. M.; McNab, H. *Synthesis* **2001**, 2059.
(195) Apeloig, Y.; Arad, D.; Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4932.
(196) Brogli, F.; Giovanni, E.; Heilbronner, E.; Schurter, R. *Chem. Ber.* **1973**, *106*, 961.
(197) Korte, S. Ph.D. Thesis, University of Köln, 1968.
(198) Neidlein, R.; Christen, D. *Helv. Chim. Acta* **1986**, *69*, 1623.
(199) Neidlein, R.; Kohl, M., personal communication, 1991.
(200) Eckert-Maksic, M.; Maksic, Z. B.; Klessinger, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 285.
(201) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.
(202) Eckert-Maksic, M.; Glasovzc, Z.; Maksic, Z. B.; Zrinski, I. *Theochem-J. Mol. Str.* **1996**, *366*, 173.
(203) Altmeyer, M.; Gaa, B.; Gleiter, R.; Rominger, F.; Kurzawa, J.; Schneider, S. *Eur. J. Org. Chem.* **2001**, 3045.
(204) Okazaki, R.; O-oka, M.; Tokitoh, N.; Inamoto, N. *J. Org. Chem.* **1985**, *50*, 180.
(205) Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 6310.
(206) Billups, W. E.; Rodin, W. A. *J. Org. Chem.* **1988**, *53*, 1312.
(207) Billups, W. E.; Chow, W. Y.; Smith, C. V. *J. Am. Chem. Soc.* **1974**, *96*, 1979.
(208) Shirafuji, T.; Nozaki, H. *Tetrahedron* **1973**, *29*, 77.
(209) Billups, W. E.; McCord, D. J.; Maughon, B. R. *Tetrahedron Lett.* **1994**, *35*, 4493.
(210) Benassi, R.; Ianelli, S.; Nardelli, M.; Taddei, F. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1381.
(211) Müller, P. *Helv. Chim. Acta* **1973**, *56*, 500.
(212) Müller, P. *J. Chem. Soc., Chem. Commun.* **1973**, 895.
(213) Halton, B.; Woolhouse, A. D.; Milsom, P. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 735.
(214) Halton, B.; Jones, C. S.; Kay, A. J.; Margetic, D.; Sretenovic, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2205.
(215) Halton, B.; Jones, C. S. *Tetrahedron Lett.* **1999**, *40*, 9367.
(216) Eaborn, C.; Eidenschink, R.; Harris, S. J.; Walton, D. R. M. *J. Organomet. Chem.* **1977**, *124*, C27.
(217) Eaborn, C.; Stamper, J. G. *J. Organomet. Chem.* **1980**, *192*, 155.
(218) Szeimies, G.; Wimmer, P., unpublished observations 1985; P. Wimmer, Diplomarbeit, University of Munich, 1985.
(219) Moore, L.; Lubinski, R.; Baschky, M. C.; Dahlke, G. D.; Hare, M.; Arrowood, T.; Glasovac, Z.; Eckert-Maksic, M.; Kass, S. R. *J. Org. Chem.* **1997**, *62*, 7390.
(220) Neidlein, R.; Constantinescu, T.; Kohl, M. *Phosphorus, Sulfur, Silicon* **1991**, *59*, 165.
(221) Neidlein, R.; Kohl, M. *Helv. Chim. Acta* **1990**, *73*, 1497.
(222) Neidlein, R.; Kohl, M.; Kramer, W. *Helv. Chim. Acta* **1989**, *72*, 1311.
(223) Kohl, M. Ph.D. Thesis, University of Heidelberg, 1990.
(224) Logan, C. F. *Tetrahedron Lett.* **1995**, *36*, 8765.
(225) Faust, R.; Knaus, G.; Siemeling, U.; Quadbeck-Seeger, H.-J. *World Records in Chemistry*; Wiley: Chichester, 1999.
(226) Chai, C. C. L.; Christen, D.; Halton, B.; Neidlein, R.; Starr, M. A. E. *Aust. J. Chem.* **1995**, *48*, 577.
(227) Okazaki, R.; O-oka, M.; Tokitoh, N.; Shishido, Y.; Inamoto, N. *Angew, Chem., Int. Ed. Engl.* **1981**, *9*, 799.
(228) Okazaki, R.; Hasegawa, T.; Shishido, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5271.
(229) Schwager, H.; Krüger, C.; Neidlein, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 65.

(230) Schwager, H.; Benn, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 67.
(231) Benn, R.; Schwager, H.; Wilke, G. *J. Organomet. Chem.* **1986**, *316*, 229.
(232) Neidlein, R.; Rufinska, A.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 640.
(233) Krüger, C.; Laakmann, K.; Schroth, G.; Schwager, H.; Wilke, G. *Chem. Ber.* **1987**, *120*, 471.
(234) Stang, P. J.; Song, L.; Halton, B. *J. Organomet. Chem.* **1990**, *388*, 215.
(235) Cotton, F. A.; Troup, J. M.; Billups, W. E.; Lin, L. P.; Smith, C. V. *J. Organomet. Chem.* **1975**, *102*, 345.
(236) Mynott, R.; Neidlein, R.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 367.
(237) Bläser, D.; Boese, R.; Brett, W. A.; Rademacher, P.; Schwager, H.; Stanger, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 206.
(238) Litosh, V. A.; Saini, R. K.; Guzman-Jimenez, I. Y.; Whitmire, K. H.; Billups, W. E. *Org. Lett.* **2001**, *3*, 65.
(239) Müller, P.; Bernardinelli, G.; Jacquier, Y. *Helv. Chim. Acta* **1988**, *71*, 1328.
(240) Maddox, M. L.; Martin, J. C.; Muchowski, J. M. *Tetrahedron Lett.* **1980**, *21*, 7.
(241) Martin, J. C.; Muchowski, J. M. *J. Org. Chem.* **1984**, *49*, 1040.
(242) Neidlein, R.; Tadesse, L. *Helv. Chim. Acta* **1988**, *71*, 249.
(243) Laue, J.; Seitz, G.; Wassmuth, H. *Z. Naturforsch. Teil B.* **1996**, *51*, 348.
(244) Kato, H.; Toda, S.; Arikawa, Y.; Masuzawa, M.; Hashimoto, M.; Ikoma, K.; Wang, S.-Z.; Miyasaka, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2035.
(245) Kato, H.; Toda, S. *J. Chem. Soc., Chem. Commun.* **1982**, 510.
(246) Nitta, M.; Sogo, S.; Nakayama, T. *Chem. Lett.* **1979**, 1431.
(247) Rubin, M. B., personal communication, 1983.
(248) Vogel, E.; Ippen, J.; Buch, V. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 566.
(249) Saito, K.; Ishihara, H.; Kagabu, S. *Bull. Soc. Chem. Jpn.* **1987**, *60*, 4141.
(250) Halton, B.; Russell, S. G. G. *Aust. J. Chem.* **1990**, *43*, 2099.
(251) Brinker, U. H.; Wüster, H. *Tetrahedron Lett.* **1991**, *32*, 593.
(252) Saracoglu, N.; Durucasu, I.; Balci, M. *Tetrahedron* **1995**, *51*, 10979.
(253) Halton, B.; Evans, D. A. C.; Warrener, R. N. *Aust. J. Chem.* **1999**, *52*, 1123.
(254) Anthony, I. J.; Wege, D. *Tetrahedron Lett.* **1987**, *28*, 4217.
(255) Kagabu, S.; Inoue, T. *Chem. Lett.* **1989**, 2181.
(256) Kagabu, S.; Saito, K.; Watanabe, H.; Takahashi, K.; Wada, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 106.
(257) Ando, S.; Imamura, J.; Tajitsu, M.; Saito, K. *Heterocycles* **1998**, *48*, 1769.
(258) Durucasu, I.; Saraçoglu, N.; Balci, M. *Tetrahedron Lett.* **1991**, *32*, 7097.
(259) Saito, K.; Ito, K.; Takahashi, K.; Kagabu, S. *Org. Prep. Proc. Int.* **1991**, *23*, 196.
(260) Neidlein, R.; Krämer, B.; Krieger, C. *Z. Naturforsch.* **1990**, *45b*, 1577.
(261) Neidlein, R.; Krämer, B. *Chem Ber.* **1991**, *124*, 353.
(262) Neidlein, R., personal communication, 1990.
(263) Saito, K.; Ando, S.; Kondo, Y. *Heterocycles* **2000**, *53*, 2601.
(264) Saito, K.; Ito, N.; Ando, S. *Heterocycles* **2002**, *56*, 59.
(265) Saito, K.; Ono, K.; Ito, N.; Tada, N.; Ando, S. *Heterocycles* **2002**, *57*, 235.
(266) Kagabu, S.; Saito, K. *Tetrahedron Lett.* **1988**, *29*, 675.
(267) Pan, W.; Jones, M.; Esat, B.; Lahti, P. M. *Tetrahedron Lett.* **1998**, *39*, 1505.
(268) Cooney, M. J.; Halton, B.; Baumgarten, M.; Gherghel, L. *Aust. J. Chem.* **1995**, *48*, 1167.
(269) Roth, W. R.; Figge, H.-J. *Eur. J. Org. Chem.* **2000**, 1983.
(270) Wentrup, C.; Müller, P. *Tetrahedron Lett.* **1973**, 2915.
(271) Wentrup, C.; Wentrup-Byrne, E.; Müller, P. *J. Chem. Soc., Chem. Commun.* **1977**, 210.
(272) Wentrup, C.; Wentrup-Byrne, E.; Müller, P.; Becker, J. *Tetrahedron Lett.* **1979**, 4249.
(273) Saunders: M.; Jiménez-Vázquez, A.; Cross, J. R.; Billups, E.; Gesenberg, C.; McCord, D. J. *Tetrahedron Lett.* **1994**, *35*, 3869.
(274) Dürr, H.; Ahr, H.-J. *Tetrahedron Lett.* **1977**, 1991.
(275) Lüddecke, E.; Rau, H.; Dürr, H.; Schmitz, H. *Tetrahedron* **1977**, *33*, 2677.
(276) Thétaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258.
(277) Yranzo, G. I.; Elguero, J. E.; Flammang, R.; Wentrup, C. *Eur. J. Org. Chem.* **2001**, 2209.
(278) Schulz, R.; Schweig, A. *Tetrahedron Lett.* **1984**, *25*, 2337.
(279) Schulz, R.; Schweig, A. *Tetrahedron Lett.* **1979**, 59.
(280) Meier, H.; Konnerth, U.; Graw, S.; Echter, T. *Chem. Ber.* **1984**, *117*, 107.
(281) Torres, M. A.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2490.
(282) Robinson, W. H.; Ditzel, E. J.; Hugel, H. M.; Kelly, D. P.; Halton, B. *J. Org. Chem.* **1981**, *46*, 5003.
(283) Fahey, J. A.; Hugel, H. M.; Kelly, D. P.; Halton, B.; Williams, J. B. *J. Org. Chem.* **1980**, *45*, 2862.
(284) Halton, B., unpublished observations, 1989.
(285) Brown, R. F. C.; Halton, B., unpublished observations, 1989.
(286) Buckland, S. J.; Halton, B.; Mei, Q.; Stang, P. J. *Aust. J. Chem.* **1987**, *40*, 1375.
(287) Ashley, K.; Sarfarazi, F.; Buckland, S. J.; Foley, J. K.; Mei, Q.; Halton, B.; Stang, P. J.; Pons, S. *Can. J. Chem.*, **1987**, *65*, 2062.
(288) Ashley, K.; Foley, K. J.; Mei, Q.; Ghoroghchian, J.; Sarfarazi, F.; Cassidy, J.; Halton, B.; Stang, P. J.; Pons, S. *J. Org. Chem.* **1986**, *51*, 2089.
(289) Halton, B.; Kay, A. J.; McNicholls, A. T.; Stang, P. J.; Apeloig, Y.; Boese, R.; Maulitz, A. H.; Hauman, T. *ARKIVOC* **2001**, *2*, 8−31, http://www.arkat-usa.org/ark/journal/Volume2/Part3/Cameron/0111/0111.pdf.
(290) Halton, B.; Kay, A. J.; McNichols, A. T.; Stang, P. J.; Boese, R.; Haumann, T.; Apeloig, Y.; Maulitz, A. H. *Tetrahedron Lett.* **1993**, *34*, 6151.
(291) McNichols, A. T.; Stang, P. J.; Halton, B.; Kay, A. J. *Tetrahedron Lett.* **1993**, *34*, 3131.
(292) Bickers, P. T.; Halton, B.; Kay, A. J.; Northcote, P. T. *Aust. J. Chem.* **1999**, *52*, 647; Halton, B.; Cooney, M. J.; Wong, H. *J. Am. Chem. Soc.* **1994**, *116*, 11574.
(293) Billups, W. E.; Litosh, V. A.; Saini, R. K.; Daniels, A. D. *Org. Lett.* **1999**, *1*, 115.
(294) Kaiser, R. I.; Bettinger, H. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2350.
(295) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, J. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
(296) Bennett, M. A.; Drage, J. S.; Griffiths, K. D.; Roberts, N. K.; Robertson, G. B.; Wickramasinghe, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 941.
(297) Roper, W. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2440.
(298) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, J. L. *J. Organomet. Chem.* **2001**, *623*, 109.
(299) Tokitoh, N. *Phosphorus, Sulfur Silicon* **2001**, *168*, 31.
(300) Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829.
(301) Dürr, H.; Klauck, G.; Peters, K.; Schering, H. G. v. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 332; *Angew. Chem. Suppl. 1983*, 347. .
(302) Wong, H. N. C.; Li, W.-K. *J. Chem. Res. (S)* **1984**, 302.
(303) Toyota, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 85.
(304) Ermer, O.; Klärner, F.-G.; Wette, M. *J. Am. Chem. Soc.* **1986**, *108*, 4908.
(305) Schleyer, P. v. R.; Jiao, H.; Sulzbach, H. M.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1996**, *118*, 2093.
(306) Carstensen-Oeser, E.; Müller, B.; Dürr, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 422.
(307) Halton, B.; McLellan, T. J.; Robinson, W. T. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1889.
(308) Neidlein, R.; Christen, D.; Poignée, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Pérez, C.; Hüber, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294.
(309) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313.
(310) Boese, R. In *Adv. in Strain in Org. Chem.*; Halton, B. Ed.; JAI Press: Greenwich, CN, 1992; Vol. 2.
(311) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.
(312) Stanger, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1988**, *53*, 4889.
(313) Burgi, H.-B.; Baldridge, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454.
(314) Frank, N. L.; Baldridge, K. K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 4389.
(315) Rathore, R.; Lindeman, S. V.; Kumar, A. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012.
(316) Shurki, A.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2205.
(317) Maksic, Z. B.; Eckert-Maksic, M.; Mo, O.; Yanez, M. In *Pauling's Legacy − Modern Modelling of the Chemical Bond*; Politzer, P., Maksic, Z. B., Eds.; Elsevier: Amsterdam, 1999; Vol. 6 and refs cited
(318) Eckert-Maksic, M.; Glasovac, Z.; Coumbassa, N. N.; Maksic, Z. B. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1091.
(319) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **2000**, *122*, 5397.
(320) Stanger, A.; Boese, R.; Askenazi, N.; Stellberg, P. *J. Organomet. Chem.* **1998**, *542*, 19.
(321) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304.
(322) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.
(323) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034.
(324) Stanger, A. International Symposium on Novel Aromatics − ISNA-10, San Diego, CA, Abstracts S59−S60, 2001.
(325) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1721.
(326) Baldridge, K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

(327) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501 and refs cited.
(328) Soncini, A.; Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. W.; Steiner, E. *J. Org. Chem.* **2002**, *67*, 4753 − we thank Prof Jenneskens for a preprint of this paper.
(329) Boese, R.; Dixon, G. M.; Halton, B., unpublished observations, 2001.
(330) Apeloig, Y.; Karni, M.; Arad, D. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Reidel: Dordrecht, 1989.
(331) Neuenschwander, M. In *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley and Sons: Chichester, 1989; Vol. Suppl. A, Pt. 2.
(332) Krygowski, T. M.; Ciesielski, A.; Cyranski, M. *Chem. Pap.* **1995**, *49*, 128.
(333) Rau, D.; Behrens, U. *J. Organomet. Chem.* **1990**, *387*, 219.
(334) Gallucci, J. C.; Kravetz, T. M.; Green, K. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6592.
(335) Hanack, M.; Ritter, K.; Stein, I.; Hiller, W. *Tetrahedron Lett.* **1986**, *27*, 3357.
(336) Harada, J.; Ogawa, K. *J. Am. Chem. Soc.* **2001**, *123*, 10884.
(337) Ogawa, K.; Sano, T.; Yoshimura, S.; Toriumi, K. *J. Am. Chem. Soc.* **1992**, *114*, 1041; Mini International Symposium On Solid State in Organic Chemistry (MIS^{3}OC) Ehime University Japan, 1993. Abstract O-9.
(338) Bonzli, P.; Neuenschwander, M. *Helv. Chim. Acta* **1991**, *74*, 255.
(339) Apeloig, Y., personal communication, 1989.
(340) Dürr, H., personal communication, 1982.
(341) Dewar, M. J. S.; Holloway, M. K. *J. Chem. Soc., Chem. Commmun.* **1984**, 1188.
(342) Billups, W. E.; Haley, M. M.; Lee, G.-A. *Chem. Rev.* **1989**, *89*, 1147.
(343) Santiago, C.; Gandour, R. W.; Houk, K. N.; Nutakul, W.; Cravey, W. E.; Thummel, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 3730.
(344) Neuenschwander, M. *Pure Appl. Chem.* **1986**, *58*, 255.
(345) Prinzbach, H.; Knothe, L. *Pure Appl. Chem.* **1986**, *58*, 25.
(346) Halton, B.; Lu, Q.; Melhuish, W. H. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 205.
(347) De Schryver, F. C., personal communication, 1996.
(348) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 445.
(349) Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912.
(350) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698.
(351) Halton, B.; Lu, Q.; Stang, P. J. *J. Org. Chem.* **1990**, *55*, 3056.
(352) Levy, G. C.; Lichter, R. L.; Nelson, G. L. Carbon-13 NMR Spectroscopy, 2nd Ed. Wiley-Interscience: New York, 1980.
(353) Koenig, T.; Curtiss, T.; Winter, R.; Ashley, K.; Mei, Q.; Stang, P. J.; Pons, S.; Buckland, S. J.; Halton, B.; Rolison, D. *J. Org. Chem.* **1988**, *53*, 3735.
(354) Singy, G. A.; Pfyffer, J.; Müller, P.; Buchs, A. *Org. Mass Spectrom.* **1976**, *11*, 499.
(355) Maksic, Z. B.; Eckert-Maksic, M.; Pfeifer, K. H. *J. Mol. Struct.* **1993**, *300*, 445.
(356) Baumgarten, M.; Halton, B.; Müllen, K., unpublished observations, 1993.
(357) Halton, B.; Halton, M. P. *Tetrahedron* **1973**, *29*, 1717.
(358) Ingold, K. U., personal communication, 1985.
(359) Warmuth, R. Personal communication, Jan. 2003; Warmuth, R.; Knobler, C. B.; Maverick, E. F.; Cram, D. J. *J. Am. Chem. Soc.* to be submitted. I thank Dr. Warmuth for making the data available.
(360) Tokitoh, N.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Takagi, N. *Organometallics* **2002**, *21*, 4309.

CR010009Z