Methylidenecycloproparenes: Novel Compounds with Fascinating Properties

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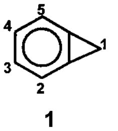
Abstract: Proton abstraction from the methylene position of a cycloproparene provides the corresponding C1 anion that can be intercepted by a carbonyl-containing compound to provide a wide range of novel methylidenecycloproparenes. The physical and chemical aspects of this comparatively new class of surprisingly stable, strained compounds have been explored. The present account provides a perspective on these developments from the initial experiments in the Utah laboratories.

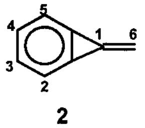
1. Introduction

Small ring compounds continue to provide a happy playground for many organic chemists not least because of the interplay between strain and reactivity.[1] The class of compounds known as the cycloproparenes[2-4] has provided a wealth of fascinating chemistry in the 30 years since the liquid parent molecule, 1*H*-cyclopropabenzene[*] (**1**) was reported by Vogel, Grimme, and Korte.[5] The strain energy of **1** has been computed[6] as 70 and measured[7] as 68 kcal mol^{-1} and approximates to this in all the simple homologues. Despite these attributes, the notoriety gained by **1** emanates more from its thiol-like malodor that is detectable at about 1 ppb; it is not surprising that the occasional laboratory misadventure, cracked or broken drainage pipes, or poor ventilation systems have provided fuel for conjecture and led to anecdotes sufficient for a winter's evening discourse! One can only speculate as to why such a simple, albeit strained hydrocarbon, is so malodorous when the individual constituents (benzene and cyclopropene) are innocuous. With such a disincentive to study it is surprising that **1** has been the subject of so many investigations, and fusion of a three-membered ring into a wide range of aromatic hydrocarbon types is now well known.[2-4]

The involvement of one of us with cycloproparene chemistry dates back many years[8] with the effect that 15 years ago our attention became focused on the wherewithal to convert the cycloproparene framework into a fully planar hydrocarbon assembly by the transformation of the sp^3 C1 center into a trigonal planar entity with stable functionality, *viz.* as an exocyclic olefin **2**. Thus 1981 saw the establishment of a collaborative venture between the Wellington and Utah groups with methylidenecycloproparenes as the common goal. Benzo-cyclopropenones, *e.g.* **3**, had been reported[9,10] but the compounds were too sensitive to both nucleophiles and electrophiles to allow for normal isolation and, while parent **3** was obtained as a transient at low temperature, matrix isolation techniques were not sufficiently well developed to allow more than infrared spectroscopic analysis.[11,12] This is a far cry from current sophistication that has allowed solution isolation and full spectroscopic characterization of ketone **3**.[13-15]



1



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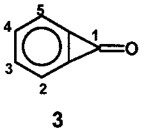

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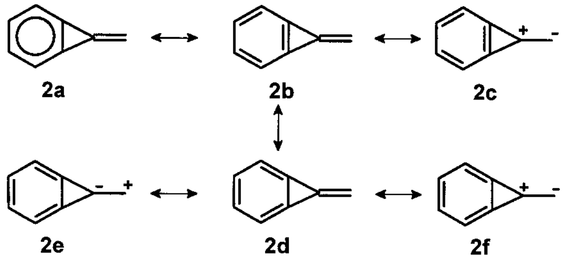
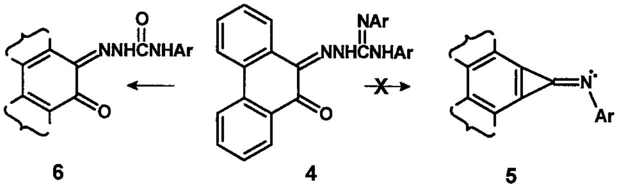
Much of the appeal of methylidenecyclopropabenzene (**2**) is displayed in its simple valence bond structures (Scheme 1) for these suggest that the compound (and its derivatives) may have chameleon character! The presence of the exocyclic double bond enables compound **2** to be viewed as a simple methylidenecycloproparene **2a**, a benzannulated methylidenecyclopropene **2b** that could exhibit triafulvene-like charge separation **2c**, or a cross-conjugated, ring-fused [3]radialene **2d** that could be polarised in either the sense **2e** or **2f** — all within the same molecule. The conversion of cycloproparene hydrocarbons into C1 olefins was first reported by us[16] in 1984 and formed the subject of a short report[17] in 1987. The present account surveys developments that have taken place in the intervening years and places particular emphasis on the physical and chemical properties of this novel and fascinating class of compounds.



Scheme 1

2. Synthesis

It so happens that the first claim[18] to the synthesis of a cycloproparene, made in 1930, was for the imine derivatives **5** formed on decomposition of the iminosemicarbazones **4** derived from 9,10-phenanthraquinone (Scheme 2). However, a reinvestigation[19] of the study failed to provide any evidence for **5**, and the only products isolated were the semicarbazones **6**. Some five years after the synthesis of **1** appeared,[5] a group of Russian workers[20] detailed the preparation of the triamine salt **7** specifically as a precursor to methylidenecyclopropa[*b*]naphthalene (**8**). However, to the best of our knowledge, the outcome of the necessary triple Hofmann elimination has not appeared in the literature even to the present time. The stage was thus set for a concerted effort to provide a viable route to the methylidenecycloproparenes.



Scheme 2

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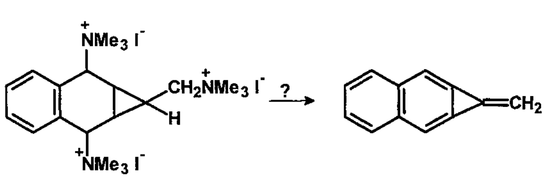
[*] IUPAC and the Chemical Abstracts Service and are unanimous in naming **1** as bicyclo[4.1.0]hepta-1,3,5-triene whereas with **14** cyclopropa fusion nomenclature applies. For the purpose of comparisons the ring system **1** is named in the text as cyclopropabenzene.



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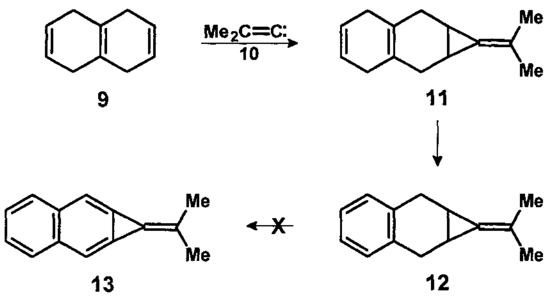
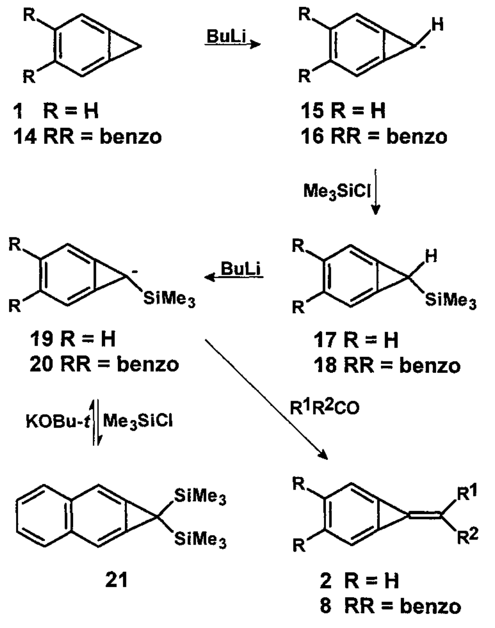
The provision of sabbatical leave enabled the New Zealand author to 'return to the bench' and in late 1981 the initial experiments began in the Utah laboratories. The study targeted the use of unsaturated carbenes[21] in the construction of the methylidenecyclopropareneframework prior to aromatization. Because strained derivatives of naphthalene are known[22] to be more stable than those of benzene, and because alkyl or aryl groups stabilize double bonds, this work was directed towards the preparation of the naphthalene derivative **13** (Scheme 3). Addition of the carbene **10** to isotetralin (**9**) provided the hexahydro-derivative **11** in accord with expectation,[23] but subsequent attempts to effect dehydrogenation led to tetrahydro **12**, polymeric material, and unchanged **11**. Furthermore, subsequent attempts to aromatize **11** with retention of the three-membered ring also failed. Clearly a different approach was needed.



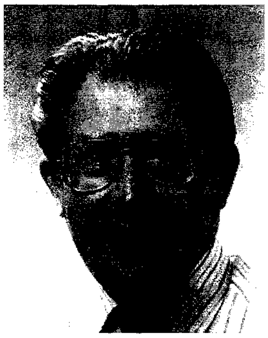
Scheme 3

The successful pathway to methylidenecyclopropanes[16] that proved subsequently to be particularly effective[24-38] commences with the preformed cyclopropane hydrocarbon and depends for its success upon the acidity of the C1 benzylic protons.[39,40] Thus deprotonation of **1** with butyl lithium provides the C1 anion **15** that is intercepted by trimethylsilyl chloride (TMSCl) to give[40] the silane **17** (Scheme 4). The facility by which silicon stabilizes an α anion[41] makes the removal of proton from **17** easier than from **2** and the α-silyl anion **19** is readily available. Capture of this by an appropriate carbonyl-containing compound in a silyl-Wittig (Peterson) olefination[42] leads to the desired methylidene derivative. In the case of **1** the entire sequence can be performed as a one-pot operation with yields of 10-38%. However, the obnoxious nature of **1** has restricted exploitation of this protocol and the range of alkylidene derivatives available is limited (Table 1). When applied to cyclopropa[*b*]naphthalene (**14**) the sequence is not as straightforward for the mono-silyl derivative **18** eludes isolation and disilyl **21** is obtained in its place (Scheme 4). This is of little consequence in the synthesis of alkylidenecyclopropanaphthalenes as **21** is readily transformed into the essential anion **20** by the action of potassium *t*-butoxide for subsequent Peterson olefination.



Scheme 4

Biographical Sketches

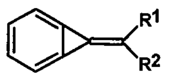


Brian Halton was born in Lancashire, England in 1941 and graduated with B.Sc (Honors) in 1963 and Ph.D. in 1966 from Southampton University and, more recently, with D.Sc. from Victoria University of Wellington. Postdoctoral studies at the University of Florida were followed by a short period as Assistant Professor before joining the faculty at Victoria University of Wellington in late 1968; he now holds the position of Professor of Chemistry. His research interests span the arena of supranatural products with emphasis among strained organic molecules for which he edits a monograph series. He has received many awards and recognitions including election to Fellowship of the Royal Society of New Zealand, has served as President of the NZ Institute of Chemistry, and was a member of the organising committee for the recent Pacifichem '95. He also holds Editorial and Advisory Board roles.

Peter J. Stang was born in 1941 in Nürnberg, Germany, raised in Hungary until 1956, and educated in the USA. He earned a B.S. degree in chemistry, magna cum laude, from DePaul University in Chicago in 1963 and a Ph.D. from U.C.-Berkeley in 1966. After NIH postdoctoral work at Princeton, he joined the faculty at Utah in 1969 where, since 1992, he holds the rank of Distinguished Professor, and served as Department Chair from 1989-1995. His research interests span reactive intermediates, like vinyl cations and unsaturated carbenes, organometallic chemistry, strained ring systems, and most recently, polyvalent iodine and alkynyl ester chemistry. His current efforts focus on supramolecular species especially via self-assembly and especially molecular squares and related macrocycles. He authored or coauthored over 290 publications including two dozen reviews and three monographs. He has been an Associate Editor of JACS since 1982 and he serves on numerous Editorial Advisory Boards. He has received many awards and honours including honorary doctorates from the Russian Academy of Sciences and Lomonosov Moscow State University.

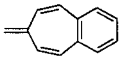
The conversion of **14** into C1 exocyclic olefins, therefore, is easily brought about by use of disilyl **21** that is itself a stable crystalline compound capable of indefinite storage in the refrigerator. As shown in Table 2, a wide range of C1 olefin derivatives is available in yields ranging from 8-95%. Moreover, the original laboratory procedures developed[24] for the preparation **21** and its subsequent transformation into derivatives of **8** have now been improved upon[32] thereby making these intriguing compounds easily available. However, it must be noted that while the use of 4-cyanobenzaldehyde as the carbonyl partner is uncomplicated,[36] the same in not the case for 4-nitrobenzaldehyde or 4,4'-dinitrobenzophenone. The sensitivity of these carbonyl compounds to base provided much frustration when attempts were made to produce a methylidene derivative carrying classical electron withdrawing functionality from their use with potassium *t*-butoxide in tetrahydrofuran. The decisive experiments that provided success came only from painstaking and systematic effort, and involved the use of both potassium fluoride and tetrabutylammonium fluoride in acetonitrile.[30]

Table 1. Methylidenecyclopropabenzenes **2** from **1** via Peterson olefination

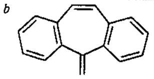


Entry	R^1	R^2	Yield %	mp °C	μ D	Ref.
1.	H	Ph	13			24
2.	H	4-$MeOC_6H_4$	31			24
3.	Ph	Ph	38	89-91	1.0	24
4.	Ph	Me	10	oil		24
5.	4-$MeOC_6H_4$	4-$MeOC_6H_4$	34	118-9	1.9	26
6.	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	24	155-7	2.2	27,28
7.	9-fluorenylidene		22	180-1	2.6	25,26
8.	benzo[*c*]cycloheptatrienylidene[a]		9	128-9		25,26
9.	dibenzo[*a,e*]cycloheptatrienylidene[b]		11	158-9	1.2	25,26

[a]



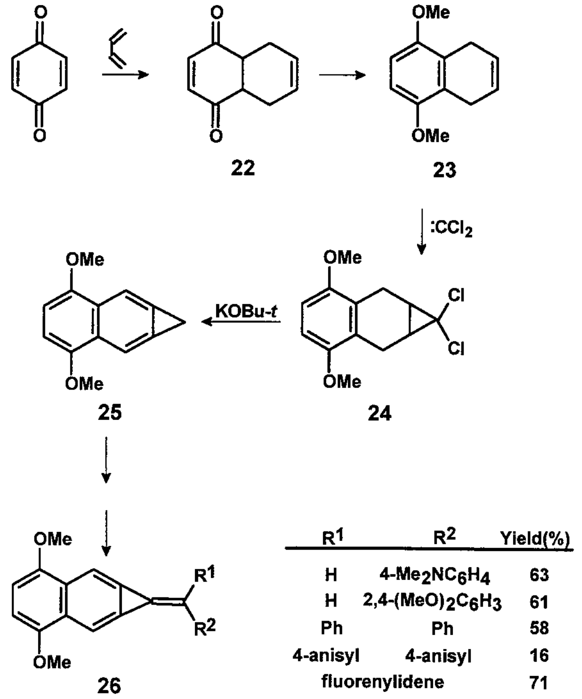
[b]



With the exception of the three oils (entry 4 of Table 1, and entries 20 and 32 of Tables 2) and the *t*-butyl derivative (entry 1, Table 2), the remaining alkylidenecycloproparenes listed in Tables 1 and 2 are remarkably air-stable, non-odoriferous, colored crystalline materials with indefinite shelf life; the di(phenylethynyl) compound (entry 23, Table 2) is very light sensitive. These compounds provide a marked contrast to many of the simple and odoriferous cycloproparene derivatives!

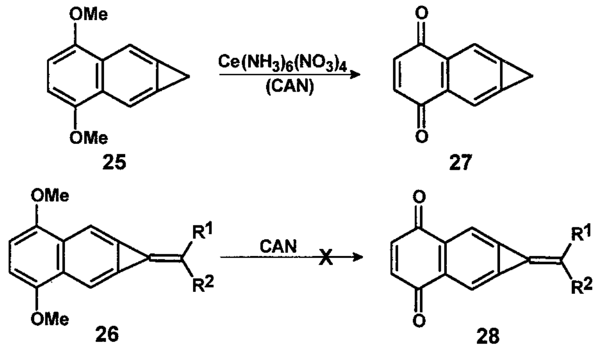
The unexpected formation of disilyl **21** described above occurs even when stoichiometric quantities of **14** and butyllithium are employed. In this instance, and with excess TMSCl, a *ca.* 6:5 mixture of **21** and regenerated **14** is obtained in 47 and 39% yield, respectively; only on one occasion was spectral evidence gleaned for monosilyl **18**.[43] More recent studies[44] aimed at intercepting anion **16** directly have also been frustrated by a high propensity for deprotonating the C1 monosubstitution product of reaction.

One can assume that the silylation protocol for methylidene synthesis will not be affected by substitution on the aromatic ring(s) providing that the functionality is stable to base. This is certainly the case for the 3,6-dimethoxynaphthalene **25**, itself prepared from 1,4-benzoquinone by way of **22-24**, as this gives[33] (via the corresponding disilyl) the methylidene derivatives **26** depicted in Scheme 5. However, the presence of the ether functionality renders the compounds somewhat air-sensitive and decomposition takes place over a period of months on standing. It is noteworthy that diether **25** undergoes oxidative de-methylation with cerium(IV) ammonium nitrate (CAN) to provide the cyclopropaquinone **27** in 85% yield; the compound is stable, red and crystalline.[33,45] Unfortunately, the olefin ethers **26** fail to behave analogously and give the attractive and extended chromophoric systems **28** (Scheme 6); while the substrates are consumed, all efforts to bring about the transformations have resulted in product mixtures that have eluded characterization.[46] In addition to these studies we must add those of Müller and his group[47] that have provided the chromium complexed methylidene **30**. The compound was obtained[48] from Peterson reaction of the complexed disilyl **29** with benzophenone but it could be characterized in solution only.

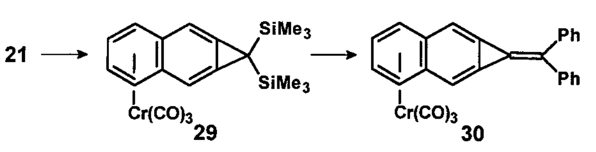


R^1	R^2	Yield(%)
H	4-$Me_2NC_6H_4$	63
H	2,4-$(MeO)_2C_6H_3$	61
Ph	Ph	58
4-anisyl	4-anisyl	16
fluorenylidene		71

Scheme 5

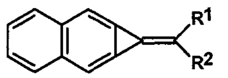


Scheme 6



Despite the successes, the olefination strategy for **1** and **14** is not without its limitations. In particular, the need to use a strong base in the formation of the essential α silyl anion **19** (or **20**) has a deleterious effect upon enolizable aldehydes and ketones; enolate ion formation competes and the yield of exocyclic olefin falls. Indeed, with acetone (and other simple aliphatic aldehydes and ketones) none of the sought after product **2** or **8** (R^1=R^2=Me) is obtained. In fact, the methodology of Scheme 4 has provided[24] only one simple alkyl-substituted exocyclic olefin, namely the naphthalene **8** (R^1=H, R^2=Bu-*t*) (entry 1, Table 2). Fortunately, the synthetic procedure of Scheme 4 is capable of adaptation by use of a modified carbonyl compound, and we were delighted to find that anion **20** undergoes nucleophilic addition-elimination with an acid chloride or acid cyanide to give the isolable C1 acyl derivatives **31** (Scheme 7).[49] As a second step addition of a nucleophile, usually as its

Table 2. Methylidenecyclopropa[*b*]naphthalenes **8** from **21** via Person olefination



Entry	R^1	R^2	Yield %	mp ^{0}C	μ D	Ref.
1.	H	*t*-Bu	68	59-60		24
2.	H	Ph	13			24
3.	H	4-$MeOC_6H_4$	31		1.4	24
4.	H	4-$Me_2NC_6H_4$	38	89-91	1.8	27,32
5.	H	4-$MeSC_6H_4$	61	137-8		34
6.	H	4-ClC_6H_4	48	154-6		26
7.	H	2,4-$(MeO)_2C_6H_3$	45	122-3		34
8.	H	2,4,6-$(MeO)_3C_6H_2$	63	114-5		34
9.	H	4-$O_2NC_6H_4$	8	193-4		30
10.	H	4-NCC_6H_4	17	187-91		36
11.	H	1-naphthyl	30	228-30		37
12.	H	2-naphthyl	43	228-30		37
13.	H	9-anthryl	45	191-2		37
14.	H	2-pyridyl	50	129-31		32
15.	H	4-pyridyl	39	183-4	3.4	32
16.	H	2-furyl	42	135-6		32
17.	H	2'-(1-methylpyrrolyl)	87	180-1		32
18.	H	2-thienyl	34	188-90	2.8	32
19.	H	ferrocenyl	66	159-60		32
20.	CF_3	CF_3	25	oil		35
21.	*t*-Bu	*t*-Bu	17	68-9		35
22.	*t*-Bu-≡	*t*-Bu-≡	73	93-4		35
23.	Ph-≡	Ph-≡	49	102-4		35
24.	Ph	Me	39	94-5		24
25.	Ph	CF_3	10			24
26.	Ph	Ph	95	110-11	0.4	24
27.	Ph	PhCO	35	83-4		35
28.	3-$CF_3C_6H_4$	3-$CF_3C_6H_4$	73	109-10		31
29.	4-$MeOC_6H_4$	4-$MeOC_6H_4$	34	118-9	2.4	26
30.	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	24	155-7	3.0	27,32
31.	4-O_2N-C_6H_4	4-O_2N-C_6H_4	84	228-9		30
32.	Ph	4-$C_6H_4S(4'$-$C_6H_4Me)$	63	oil		32
33.	Ph	2-thienyl	52	55-7		32
34.	2-thienyl	2-thienyl	59	94-5	9.1	32
35.	9-fluorenylidene		22	180-1		26
36.	9-(10,10-dimethyl)anthrylidene^a		63	153-5	1.7	37,38
37.	9-(*N*-methyl)acridinylidene^a		22	178-9		38
38.	9-xanthenylidene^a		59	219-21		38
39.	9-thioxanthylidene^a		46	171-3		38
40.	9-anthronylidene^a		35	248-50		37,38
41.	benzo[*c*]cycloheptatrienylidene^b		9	128-9		25,26
42.	dibenzo[*a, e*]cycloheptatrienylidene^c		11	158-9		25,26

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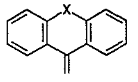

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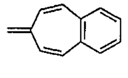

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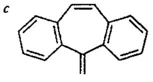
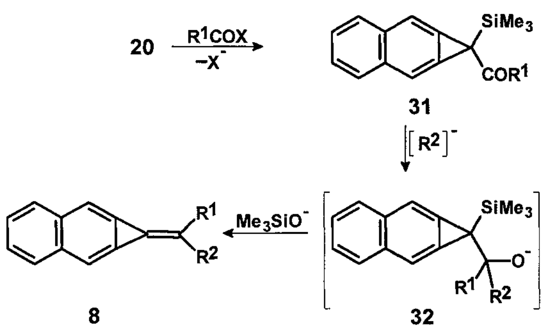


lithium salt, triggers formation of oxyanion **32** that undergoes Peterson olefination and provides simple alkylidenecyclopropa[*b*]naphthalenes **8** with hitherto unavailable functionality at the exocyclic center. While the range of compounds prepared by this procedure is limited to those given in Table 3 they represent the simplest substituted alkylidenecycloproparenes so far obtained. The reaction conditions necessary to give viable quantities of **31** and then derivatives of **8** by this route require rigorous drying of reagents and solvents, and this adaptation has yet to be tested in the cyclopropabenzene (**1**) series.

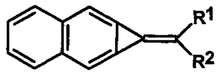


Scheme 7

Although the methodologies summarized above have provided us with some 60 compounds neither of the parent (unsubstituted) exocyclic olefins **2** or **8** (R^1=R^2=H) have emerged despite our best efforts; these highly desirable compounds thus remain a challenge for the synthetic chemist. However, evidence for parent **2** does exist. Vogel and his colleagues[50] have found that flash vacuum pyrolysis (fvp) of **33** affords *o*-dicyanobenzene and phenylethyne. The most logical explanation for obtention of alkyne requires the intervention of **2** as shown in Scheme 8.

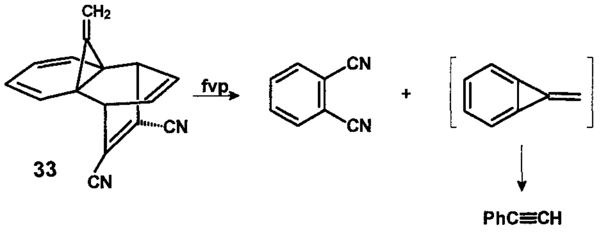
It should not be presumed that synthetic work in this area is restricted to

Table 3. Alkylidenecyclopropa[*b*]naphthalenes **8** from **31** via Peterson olefination^a



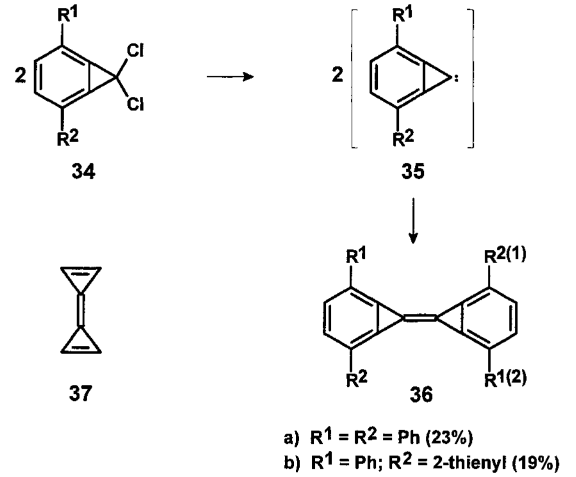
Entry	R^1	R^2 %	Yield ^{0}C	mp
1.	H	Me	41	65-7
2.	Me	Me	54	88-9
3.	Et	Et	55	95-6
4.	OMe	OMe	52	81-3 (dec.)
5.	OMe	NMe_2	43	61-2 (dec.)
6.	OMe	CN	62	78-80
7.	NMe_2	NMe_2	60	76-9 (dec.)
8.	NMe_2	CN	36	69-71
9.	NPh_2	NPh_2	65	98-100

^{a}Data taken from reference 49.



Scheme 8

our own laboratories. While the complexed methylidene **30** was referred to earlier, Neidlein and co-workers[51] have effected cycloproparenylidene dimerization as shown by the transformation **34**→**36**. The reaction is limited by the availability of appropriate carbene precursors and to date only the two derivatives shown in Scheme 9 have been characterized; to the best of our knowledge these structures represent the only examples of the unusual and fascinating C_6H_4 triafulvenylidene skeleton **37**. Attempts to extend these latter studies into the naphthalene series have met with mixed success.[38] By use of the known[52] benzo analogue of **34a** a deep red material was formed and, while it is presumed to be the analogue of **36a**, the compound is both air and light sensitive and has eluded characterization. Other plausible pyrolytic pathways to **2** have been examined[11,53,54] and, while the outcomes have been established, they provide notably less evidence for the involvement of the compound and do not justify further discussion here.[2]



Scheme 9

3. Physical Properties and Theoretical Considerations

Almost all of the methylidenecycloproparenes are colored crystalline compounds that show remarkable thermal stability and appear to have indefinite shelf life; the exceptions are found with the exocyclic vinyl ethers and enamines of Table 3. From the valence bond structures depicted in Scheme 1 the various hydrocarbons that have been made may be viewed simultaneously as novel examples of both methylenecyclopropene[55-59] and [3]radialene (trimethylenecyclopropane),[60,61] and this has triggered a detailed assessment of their physical characteristics encompassing strain energies, polarities and structures as these are critical indicators. While much essential information has been gained there remains a range of measurements yet to be recorded.

Early computations of the resonance energies and structures of a number of benzannelated methylidenecycloproparenes were made[62] but the results have been superseded by calculations at the *ab initio* [HF/STO-3G, HF/6-31G(d,p) and MP2/6-31G(d,p)] and semiempirical (PM3) levels of theory.[6,63-67] At the time when computational chemistry was restricted to comparatively few exponents a stimulating and ongoing collaboration developed with Apeloig and his students in Haifa.[6,63-65] Only with developments in hardware and software did the cycloproparenes succumb to detailed theoretical assessment and provide reliable information.[6,63] Indeed, in the early days many of the computations were restricted to vacation periods when the Technion computer was not too busy with administrative chores; after all **1** (C_7H_6) was a large molecule in those days! To our joy meaningful information on the geometry and strain energy of **1** emerged[6] and comparable data for **2** followed using the minimal STO-3G basis set.[65] The calculations have been repeated and extended through an enlarged collaboration that encompasses the crystallographic and theoretical acumen of Boese in Essen. Methylidenecyclopropabenzene (**2**) is *ca.* 2 kcal mol^{-1} *less* strained than **1** (68 *vs* 70 kcal mol^{-1}) and this gain in the stability of **2** is ascribed to polarization within the molecule; a dipole moment of 1.2 D is predicted to lie in the direction of the exocyclic C6 center. Calculations at the HF/STO-3G level provide dipole moments best in agreement with the experimentally determined values of Tables 1 and 2, while geometrical parameters at the HF/6-31G(d,p) level are more consistent with X-ray results (see below). Relevant bond lengths and interbond angles calculated for **1** and **2** as well as the crystallographic values[68] for **1** are shown in Figure 1.

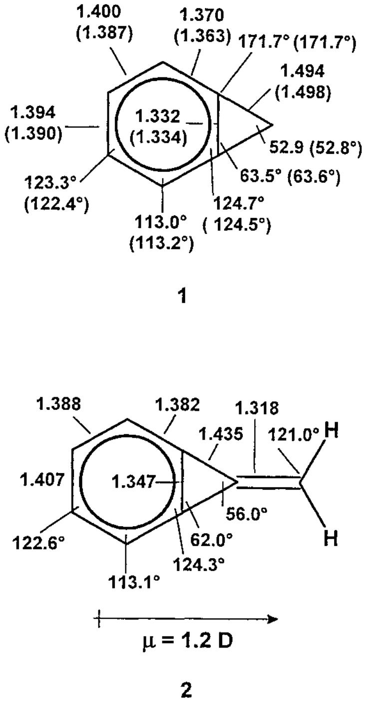


Figure 1. Calculated and experimental geometry of **1** and calculated geometry of **2**. X-Ray data for **1** are in parenthesis and bond lengths are in Å and angles in degrees (°).

The availability of fluorenylidene and cycloheptatrienylidene derivatives of **2** and **8** (Tables 1 & 2; unsubstituted parents are not known) prompted comparable investigations[65,67] of the cross-conjugated fulvalene derivatives of **2** that result from fusion of a π-conjugated cyclic hydrocarbon to the terminal position of the exocyclic olefin. Thus HF/STO-3G calculations on triafulvene **38**, calicene **39** and triaheptafulvene **40** have been performed[65,67] and as shown in Figure 2 the direction of the dipole in **38** is the *opposite* to that in **2** or **39**. The expectation of a polarity in **2** directed towards the exocyclic C6 center has analogy with methylidenecyclopropene.[55-58] Moreover, a dipole directed towards the five-membered ring of **39** meets expectations as it is nicely compatible with development of cyclopentadienyl anion character from an electron donating cyclopropabenzenyl moiety; a significant contribution to the structure from the polar form is to be expected. As it so happened, the permanent dipole moments of fluorenylidene **41** and cycloheptatrienylidene **42** had been obtained[26] from capacitance measurements using the procedures of Guggenheim[69] with classical methodology[70] but employing a small (*ca.* 2 mL) homemade capacitance cell; values are 2.6 and 1.2 D, respectively. The repeated use of appropriate standards allows for confidence in the permanent dipole moments that have been recorded this way (Tables 1 & 2), and we conclude that many of the compounds do indeed have such dipoles whose magnitudes are mollified in comparison to many fulvenes and fulvalenes by the fusion of the aromatic ring to give the cycloproparenylidene substructure. Indeed, the obtention[26] of a value of 1.2 D for cycloheptatrienylidene **42** was met with much enthusiasm as a contribution to the structure of **42** from the cycloheptatrienyl cation seemed to provide the necessary evidence to suggest ambiphilicity of the cyclopropabenzenylidene unit, *viz.* opposing directions of polarity in **41** and **42** in accord with obvious expectations. However, experiment provides the *magnitude* and not the *direction* of the permanent dipole. The direction comes from intuition, by analogy, or (nowadays) more reliably from calculation. That **40** is predicted to have its dipole directed *towards* the seven-membered ring provided a salutary lesson, and compound **42** is presumed to have its polarity directed in the same direction! The computations thus dictate that the cyclopropabenzenylidene moiety is a stronger electron donor than cycloheptatrienylidene.

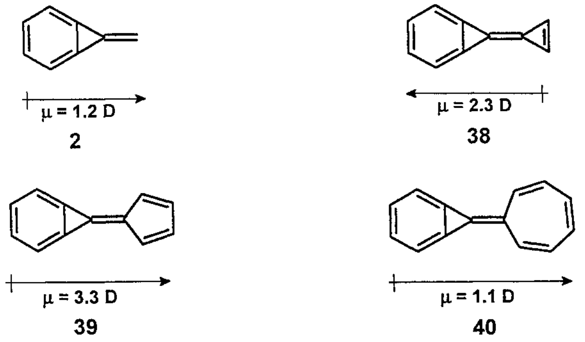
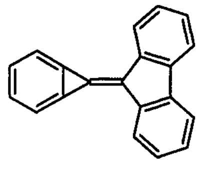
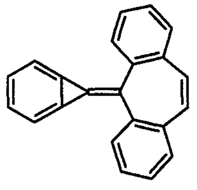


Figure 2. Calculated dipole moments (HF/STO-3G) for selected methylidenecycloproparenes.

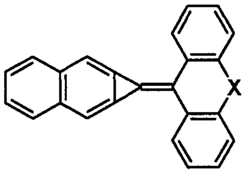
The impact of the above is for the conjugated seven-membered rings of **40** and **42** to have 8π character. For **42** this manifests itself in a puckered, non-planar structure (see below).



41 μ(meas) 2.6 D
μ(calc) 2.6 D

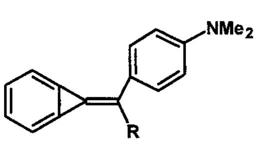


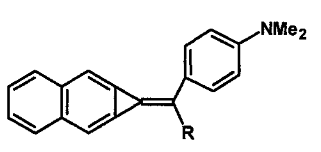
42 μ(meas) 1.2 D
μ(calc) 1.3 D



43 a) X = CMe2
b) X = O
c) X = S
d) X = NMe
e) X = CO

While PM3 and STO-3G procedures provide dipole moments of comparable magnitude to the measured values, all of the basis sets employed give dipoles that place the compounds in the same relative order. What is of paramount importance from the calculations is that triafulvene **38** is the *only* one of the hydrocarbon ring systems to have its dipole directed towards the six-membered ring. To date, the only known compounds with this ring system[51] are the cycloproparenylidene dimers **36** as reactions between anion **20** and various cyclopropenones fail to deliver the sought-after materials;[35,38] much more concerted effort will be needed before the outcomes are established.





44 a) R = H **45**
b) R = 4-Me$_2$NC$_6$H$_4$

It is presumed that each of the anthrylidene derivatives **43** (entries 36-40, Table 2)[38] are polarized and the dipole is expected to be directed towards the cyclopropanaphthalenyl moiety in **43b-d** as these molecules carry typical electron donating heteroatoms. Polarity in anthronylidene **43e** with the electron withdrawing carbonyl group at C10′ is expected to be in the reverse direction. Unfortunately, only the 10,10-dimethyl derivative **43a** is sufficiently soluble for capacitance measurement and dipole determination; a value of 1.7 D is recorded[37] (entry 36, Table 2). With electron donating *p*-dimethylaminophenyl groups compounds **44** and **45** are presumed polar and this is established[27] for **44b**, and **45a** and **b** (entry 6, Table 1, and entries 4 and 30, Table 2, respectively). It must be stressed that the theoretical study has not yet been extended to encompass the range of methylidenecyclopropa[*b*]naphthalenes studied and subjected to x-ray crystallographic analysis.

As intimated above crystallographic studies have been carried out on a range of methylidenecycloproparenes[24,32,66,67,71,72] and several of the structures have been replicated theoretically.[66,67] The best correlation with the x-ray results occurs for computations at the HF/6-31G(d,p) level of theory rather than from the inclusion of correlation effects by the MP2 procedure;[67] MP2 optimized bond lengths are almost 0.02 Å longer than the HF and experimental values. Selected bond lengths and interbond angles for the range of structures that have been examined are presented in Table 4, and for completeness the calculated data for **2** (entry 1) and **38** (entry 3) are also appended; the crystal quality of the thienyl derivative **46** has resulted in high uncertainties. The impact of incorporating an exocyclic double bond at C1 of a cycloproparene on the cycloproparenyl moiety has been presented[71] for **45a** and **b** and the detailed discussion is not repeated here. While all of the compounds studied show remarkable similarity among the interbond angles (Table 4), it is important to note that angles α and ß of the three-membered ring are widened and narrowed by *ca.* 3° and 2° with respect to the parent cycloproparene hydrocarbon (**1**:[68] α=52.8°, ß=63.6°; **14**:[73] α=54.2°, ß=62.8°) and this is nicely consistent with the changes associated with C1. Moreover, the bridge bond (bond *c*, Table 4) is *longer* than that in parent **1** (1.334 Å)[68] or **14** (1.375 Å),[73] respectively, while the lateral cyclopropane σ bonds (bonds *b*, Table 4) are *shorter* than those in the

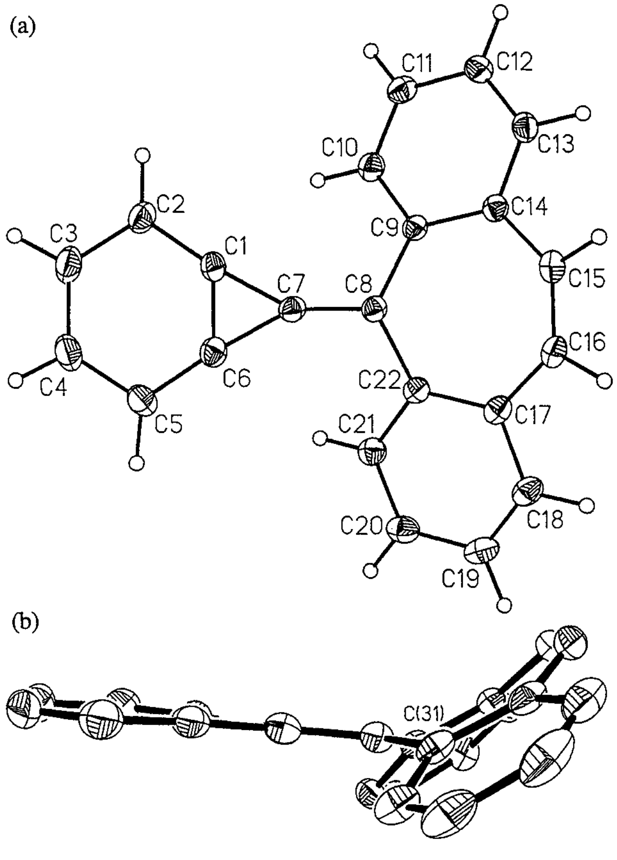
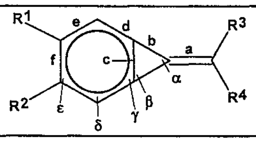


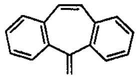
Figure 3. X-Ray structure of compound **42** (a) from above and (b) in the plane of the cyclopropabenzenylidene moiety.

Table 4. Experimental and calculated structural data for selected methylidenecyclopropanes (bond lengths in Å and angles in °)

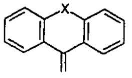


Entry	R^1	R^2	R^3	R^4	method	*a*	*b*	*c*	*d*	*e*	*f*	α	β	γ	δ	ϵ	Ref.
1.	H	H	H	H	calc.	1.318	1.435	1.347	1.382	1.388	1.407	56.0	62.0	124.3	113.1	122.6	67
2.	H	H	Ph	Ph	x-ray	1.343	1.433	1.355	1.379	1.384	1.388	56.4	61.8	124.0	113.0	123.0	24
3.	H	H	cyclopropenylidene		calc.	1.309	1.433	1.363	1.363	1.411	1.324	56.5	61.7	124.3	112.8	122.8	67
4.	H	H	fluorenylidene		x-ray	1.338	1.440	1.377	1.382	1.400	1.410	57.1	61.5	123.7	113.6	122.7	67
					calc.	1.331	1.425	1.347	1.384	1.386	1.410	56.4	61.8	124.4	112.9	122.8	67
5.	H	H	dibenzo[*a,e*]cycloheptatrienylidene[a]		x-ray	1.347	1.436	1.376	1.382	1.399	1.397	57.0	61.5	124.1	113.1	122.9	67
					calc.	1.345	1.431	1.341	1.382	1.389	1.406	56.2	61.9	124.4	113.8	122.7	67
6.	benzo		fluorenylidene		x-ray	1.346	1.430	1.390	1.362	1.423	1.451	58.2	60.9	124.4	114.3	121.3	67
					calc.	1.329	1.427	1.374	1.353	1.426	1.431	57.6	61.2	124.7	114.0	121.3	67
7.	benzo		9-(10,10-dimethyl)anthrylidene[b]		x-ray	1.348	1.432	1.388	1.349	1.424	1.450	58.0	61.0	124.5	114.6	120.9	72
8.	benzo		9-(*N*-methyl)acridinylidene[b]		x-ray	1.360	1.427	1.396	1.354	1.439	1.442	58.6	60.7	124.5	114.5	121.1	72
9.	benzo		9-thioxanthylidene[b]		x-ray	1.344	1.437	1.380	1.351	1.429	1.450	57.4	61.3	124.8	114.2	121.0	72
10.	benzo		H	thienyl	x-ray	1.351	1.403	1.381	1.400	1.462	1.498	58.7	61.1	127.7	114.6	121.0	32
11.	benzo		H	4-$Me_2NC_6H_4$	x-ray	1.329	1.448	1.395	1.346	1.433	1.440	57.7	61.1	124.2	114.7	121.0	32
12.	benzo		4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	x-ray	1.346	1.445	1.399	1.349	1.445	1.431	58.1	60.0	124.3	114.4	121.3	32

[a]



[b]



cycloproparene homologues (**1**: 1.498; **14**: 1.503 Å). Again, this is consistent with the presence of the exocyclic double bond. Of the compounds in the cyclopropabenzene series, triafulvene **38** is the only compound expected to have the exocyclic bond (bond *a*, Table 4) *shortened* in comparison to **2**; the other three have this bond longer with little variation between them. In the cyclopropanaphthalene series the exocyclic double bond (bond *a*, Table 4) varies in the range 1.329-1.360 Å and, while the bridge bonds are longer than that in **14**, the differences are notably smaller than those recorded for the methylidenecyclopropabenzenes. Only the geometry of one cyclopropanaphthalene derivative, the fluorenylidene, has been the subject of theoretical assessment.

All of the methylidenecycloproparenes examined crystallographically retain the essential planarity of the cycloproparenyl moiety and have the three-membered ring bent out of the plane of the aromatic unit by the same 2-3°. In the fulvalene series the fluorenylidene derivative **41** and its naphtho analogue are almost planar throughout while the cycloheptatrienylidene **42** (Fig. 3) has the remote C=C twisted out-of-plane by *ca.* 28°. As discussed above this puckered structure likely results from a resistance of the molecule to 8π antiaromatic electron delocalization. The anthrylidene derivative **43a** has the central anthracenyl ring in a boat conformation (Fig. 4a) but upon replacement of the sp^3-hybridized C10 by a heteroatom the structure becomes essentially planar as shown by **43b** and **d** (Figs. 4b and 4c) and mesomerism is possible throughout each of these two molecules.

In the fulvene series the independent substituents at the exocyclic center almost attain planarity when one is a hydrogen atom. Thus the mono(dimethylaminophenyl)- and thienyl-methylidene derivatives **45a** and **46**, respectively, have the pendant 6π6C and 6π4CS aromatic rings twisted from planarity by only *ca.* 5° as shown for the latter in Figure 5. In comparison, one finds that in diaryl **45b** the substituted phenyl rings are rotated out of plane by about 28°. These values are markedly *less* than the values of 37-45° recorded for comparably substituted hepta-[74] and pentafulvenes,[75] *e.g.* 44.8° for **47**, but are akin to the values determined for a range of (*E*)-stilbenes.[76,77] Thus the twist angles of *ca.* 5° recorded for **45a**, and **46** match those for the phenyl rings in (*E*)-stilbene itself, while those of **45b** compare well with *o,o'*-dimethyl-substituted (*E*)-stilbenes (*ca.* 25°) and not the values of 45-50° between the substituents recorded for 1-chloro-1,2,2-triphenylethene.[77] The data are consistent with enhanced steric freedom about the exocyclic double bond because of the presence of the fused three-membered ring — with hindsight we are reminded that the methylidenecycloproparenes represent stable derivatives of 1,6-didehydrocycloheptatriene! A likely consequence is mesomerism because of plausible π orbital overlap thruout the molecule. There is no necessity to invoke polarisation of the exocyclic π bond by the *ipso*-carbon atom of the 6π6atom or 6π5atom substituents, a necessary feature when twist angles are large.[74,78] Moreover, the detailed data obtained for **45a** and **b** support the assumption that the dipoles in these molecules are directed towards the cycloproparenyl moiety as expected. The lower crystal quality of **46** has prevented analogous analysis and the thienyl moiety is presumed to be the electron donor (μ 2.8 D). The important feature here is the demonstration of a near planar molecule.

The spectroscopic properties of the methylidenecycloproparenes are of particular interest and reflect the polarity present in this family of compounds. The infrared spectra of the compounds show characteristic stretching frequencies[17] in the ranges 1760-1790 and 1510-1550 cm^{-1} that relate to those of 1810-1880 and 1510-1550 cm^{-1} for methylenecyclopropene derivatives[79] and with the values 1770 and 1519 cm^{-1} for the parent itself.[55-58] It seems likely that these bands result from strong coupling between the endocyclic (aromatic) and exocyclic double bonds and the shift to lower wavenumber of the high energy transition is consistent with the polar structures recorded. The electronic absorption spectra of the aryl-substituted methylidenecycloproparenes display long wavelength maxima that account for their color. The positions of these maxima are solvent dependent and are moved to *shorter* wavelengths by 5-7 nm when the solvent polarity is increased. These small shifts are in the opposite sense to that expected for a $\pi \rightarrow \pi^*$ transition but such negative solvatochromy is typical of other polar fulvenes and fulvalenes.[80] Indeed, the mesomerism present in *e.g.* **45b** can be removed by quaternization of the dimethylamino groups and when this is done the UV absorption maximum reverts to that of the unsubstituted diphenyl derivative.[27] The dyes that are formulated around the anthrylidene substructure, *viz.* **43**, have colors that range from yellow (**43a**) to orange (**43b**) to red (**43c**) and violet (**43d**). However, it was not so much the absorption spectra that gained our attention as much as the emission spectra of this range of compounds. During the isolation of the dimethylaminophenyl derivatives, and especially **45a**, it became abundantly obvious that the extended conjugation and the nature of the substituents provided a notable lumophore.

Emission spectroscopy has established[2,81] that the phenyl substituted methylidenecycloproparenes of Tables 1 and 2 are markedly more fluorescent than their parents and that the 6π5atom heterocyclic analogues also fluoresce. The absolute quantum yields for the fluorescence of **45a** and **b** are 0.96 and 0.81, respectively.[81] The absorption/emission characteristics of **45a** are shown in Figure 6. More recent measurements[82] on

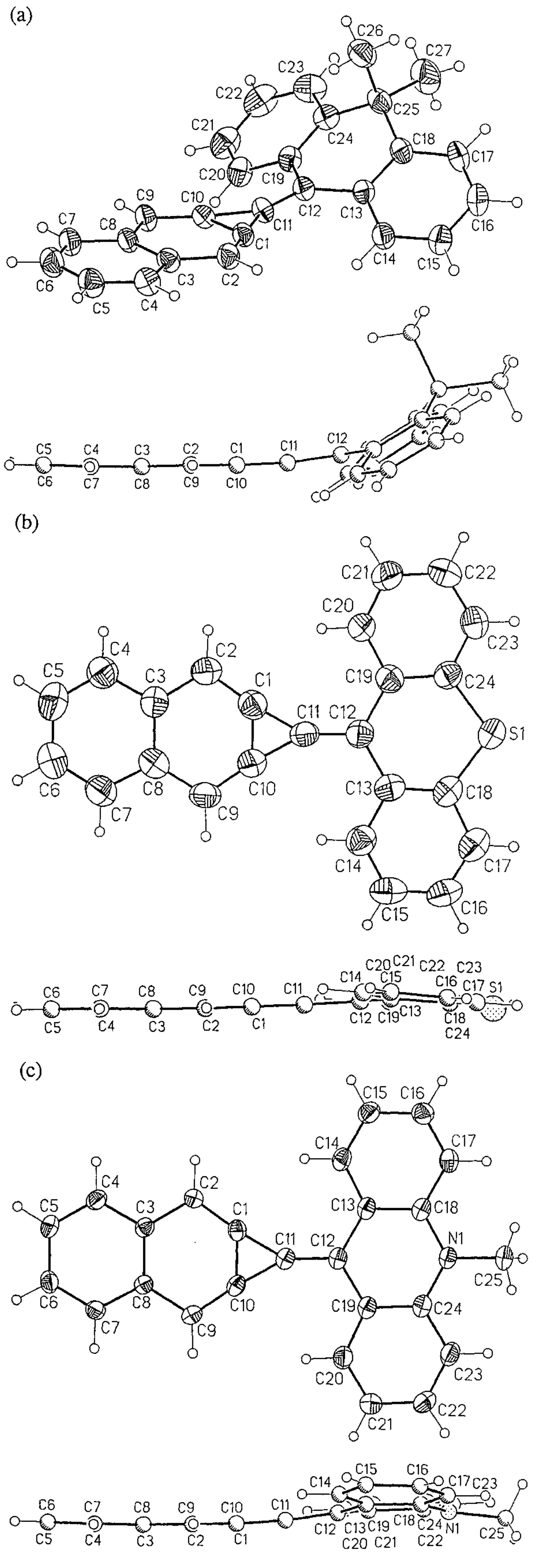
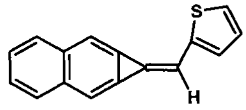


Figure 4. X-Ray structures of (a) **43a**, (b) **43b** and (c) **43d** from above and in plane with the cycloproparenylidene moiety.



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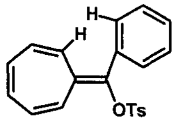


47

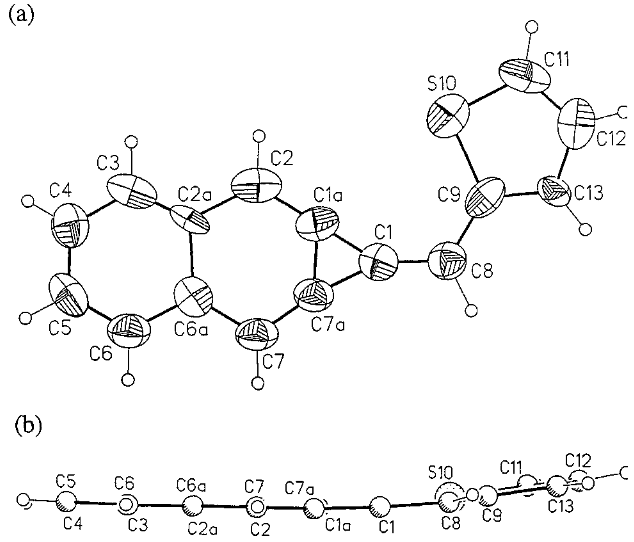


Figure 5. X-Ray structure of thienylmethylidene **46** (a) from above and (b) in the plane of the cycloprparenylidene moiety.

this compound in a range of solvents have shown that the stationary excitation spectra are independent of the emission wavelength and the same as the absorption spectra. The quantum yield is between 0.9 and 1.0 and the fluorescence maximum varies from 474 nm in isooctane to 543 nm in acetonitrile. Despite the fact that the first obviously fluorescent compound, *viz.* **45a**, was of serendipitous origin, subsequent deliberate attempts to provide other stable derivatives with similar fluorescence characteristics have been singularly unsuccessful; the pyrrolyl analogue (entry 17, Table 2) is comparable but the compound is much less stable!

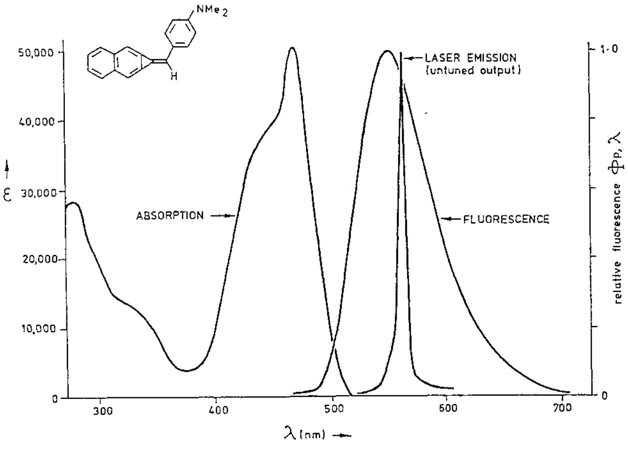


Figure 6. Absorption-emission spectra of **45a** in dimethylformamide

The NMR spectra of the methylidenecycloproparenes,[17] like the parent compounds,[2-4] provide for easy recognition of the compounds. The proton spectra can show overlapping signals when 6π6atom and 6π5atom exocyclic substituents are present. However, the presence of *para*-coupled doublets (*J* ~ 1.5 Hz) (monosubstituted derivatives) or a sharp singlet (symmetrical derivatives) in the aromatic region is often discernable. These signals are due to the protons adjacent to the sites of the three-membered ring fusion, *viz.* H2/5 in **2** and H2/7 in **8**, and their presence characterizes the compounds. Furthermore, the symmetrically substituted compounds of Table 3 not only show this signal but also a clearly discernable AA'BB' pattern for the H3-H6 protons of the remote six-membered ring.

The ^{13}C NMR spectra of the series of compounds provide the most useful information. In particular, the carbon atoms adjacent to the fusion sites of three-membered ring are typically shielded[2-4] and appear in the range 96-115 ppm. This likely results from the bent bonds to these centers caused by fusion of the cyclopropene ring. These signals are diagnostic for cycloproparene presence and their assignments are confirmed from ^{1}H-^{13}C 2D COSY experiments. The signals for the exocyclic double bond carbon atoms are usually distinguishable and fall in the range 100-120 ppm. More importantly, the chemical shifts of the various carbon atoms of **2** and **8** that carry a *para*-substituted aryl group at the exocyclic center (C6 of **2** and C8 of **8**) are systematically influenced by the nature of the substituent and an excellent correlation exists[28,29] between δ and σ_p^+, the Hammett constant that best represents resonance contributions. As the correlations of the cycloproparenyl and exocyclic alkene carbon atoms with σ_p^+ have been depicted in graphical form and discussed elsewhere,[29] all that is provided here are updated illustrations (Fig. 7) of the dependence of C2 on σ_p^+ for derivatives of **8** carrying one and two C8 aryl substituents. It is concluded that the ^{13}C chemical shifts of **2** and **8** reflect the electron donating or withdrawing nature of the remote aryl substituent and support further our contention that mesomerism is important in this family of compounds. As discussed above, the presence of small twist angles in the methylidene compounds allows for mesomeric influence and argues against polarization concepts.

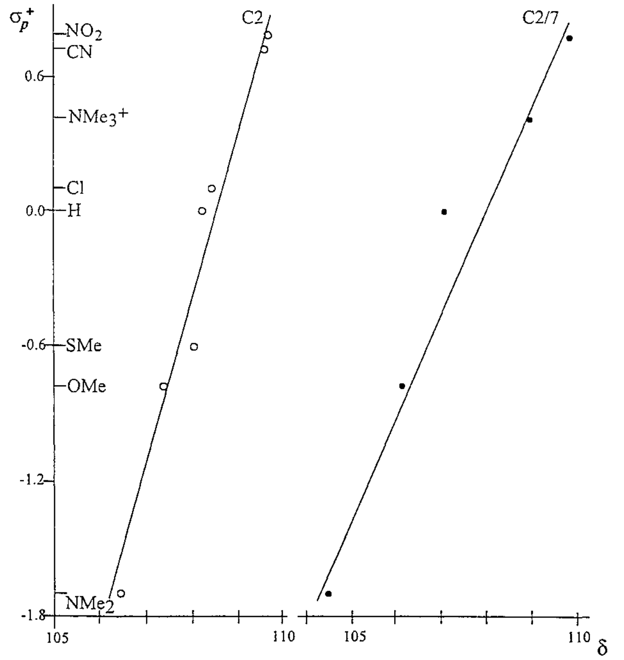
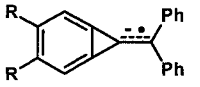
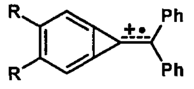


Figure 7. ^{13}C NMR correlations for monoaryl- (C2) and diaryl-(C2/7) methylidenecyclopropa[*b*]naphthalenes.

Electrochemical and spectroelectrochemical investigations of the diphenylmethylidene compounds (**2** and **8**; R^1=R^2=Ph) have shown that each affords a stable radical anion (λ_{max} 519 and 587 nm, respectively) and a quasi-stable radical cation.[83,84] As the reduction and oxidation steps are reversible the ring system is likely retained; structures **48** and **49** are therefore proposed for these species. The studies also revealed a difference between the half-wave oxidation potential ($E_{½}^{+}$) to give **49a** (0.68 eV) and **49b** (0.81 eV). This ordering is contrary to the norm whereby the more delocalized system (**8**; R^1=R^2=Ph) is the more easily oxidized. Consequently, the photoelectron spectra of these two diphenylmethylidene derivatives were recorded and show[85] that the observed differences in the $E_{½}^{+}$ values have no clear counterpart in the gas phase — the first ionization potential of the two compounds is essentially the same. This applies to both the first peak maximum [~IP(vertical), 7.14(5) eV] and the onset [~IP(adiabatic), 6.84 eV]. The differences in the $E_{½}^{+}$ values have been ascribed therefore to structure-specific solvation effects. The impact of the fused three-membered ring on the ionization energies is small and manifests itself by a reduction of *ca.* 0.2 eV in the second and higher ionization energies.


48

a) R = H
b) RR = benzo


49

The various data recorded for the methylidenecycloproparenes provide no evidence to support a bond localized structure[86] as might be expected on the basis of the Mills-Nixon hypothesis[87] The simple valence bond picture of a molecule oscillating between a ring fused triafulvene (**2b**) and a novel radialene (**2d**) has clear aesthetic appeal, but it bears little resemblance to the reality that derivatives of **2** and **8** are markedly distorted, highly strained, but surprisingly stable compounds. The cycloproarenyl moiety therein is demonstrably ambiphilic as it will accept or donate electron density depending upon the nature of the substituents attached to the exocyclic double bond.

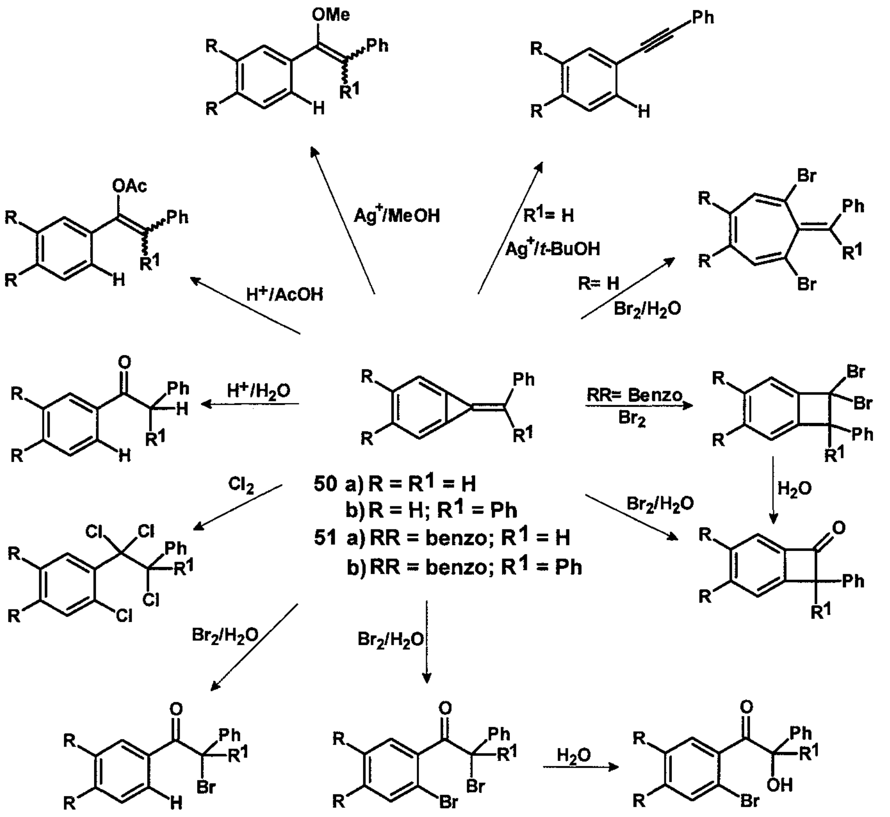
4. Chemical Properties

The methylidenecycloproparenes are much more sensitive to electrophiles[88] than to nucleophiles[89] and a rapid reaction occurs in the presence of simple acids that results in opening of the three-membered ring. While one might imagine the chemistry to be dominated by such ring cleavage, this is only true when the conditions permit it; the fact of the matter is that under appropriate aprotic conditions the ring system is surprisingly stable. Indeed, we were most surprised to find that the diphenylmethylidene **50b** is recovered unchanged from several days in refluxing toluene.[90] Consequently, much of the stimulation and fascination of these compounds has (and continues to) come from the prospects of utilizing their thermal stability and unusual structure in the synthesis of otherwise inaccessible compounds.

Despite the number of derivatives that are now available it is unfortunate that there has been no systematic study of the interaction of the methylidenecycloproparenes with electrophilic species. Rather, the first compounds to be obtained were examined[88] and as much of this chemistry has been presented already[2,17] it is simply summarized here and shown in Scheme 10. In general, an electrophile is captured at the exocyclic center to provide an intermediate cycloproparenyl cation and this appears to be the case even when the substituent at this site is electron donating. Thus the anisyl derivative shown in Scheme 11 gives rise to a 1,2-diarylethanone.[37] However, on complexation with Ag(I) cleavage of the strained three-membered ring σ bond occurs (Scheme 10) in direct analogy with the simple cycloproparenes.[91,92] The addition of bromine to the bridge bond rather than the exocyclic olefin occurs only in the cyclopropabenzene series and is followed by ring expansion of the norcaradiene into the heptafulvene series (Scheme 10). Analogous reactions for the naphthalene homologues avoid the high energy orthoquinodimethane intermediate that would result from addition across the bridge bond (see below) and involvement with the exocyclic double bond leads to subsequent opening of the three-membered ring.[88]

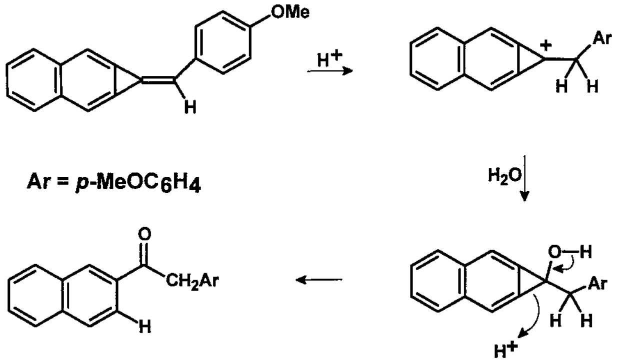
The synthetic protocols for the methylidenecycloproparenes provide the compounds in strongly basic media. It is not surprising, therefore, that they are resistant to nucleophilic attack. In fact, reactions in the benzene and naphthalene series, *e.g.* **50a** and **51a**, with *t*-butoxide ion in tetrahydrofuran require several days of reflux, and lead to a heptafulvene in both cases by way of ring expansion from addition across the bridge bond (Scheme 12).[89]

Because the HOMO of a cycloproparene is located at the bridge bond the compounds behave as electron rich dienophiles in inverse electron demand Diels-Alder cycloadditions. The result is a ring fused norcaradiene that frequently proceeds to a methanoannulene framework depending on the precise cycloaddition partners involved.[2,92-95] In contrast, the methylidenecycloproparenes present the exocyclic double bond as an alternative reaction center and a key question that had to be addressed was at which of the two sites would reaction occur — involvement of

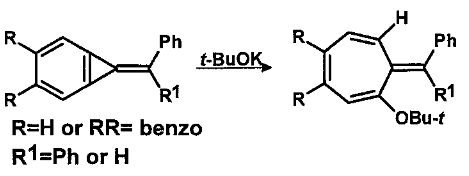


Scheme 10

the exocyclic double bond would lead to unusually fused spirocycles while reaction with the bridge bond could give novel methylidene-bridged annulene derivatives. The simple argument that addition to the bridge bond of the naphthalene derivatives (**8**) requires loss of aromaticity in *both* of the six-membered rings and gives rise to a high energy orthoquinodimethane intermediate clearly supports reaction at the exocyclic double bond. However, this argument has no substance when applied to methylidenecyclopropabenzene derivatives and [4+2] Diels-Alder reaction seemed possible at either site. FMO analysis[96] provided little assistance as the HOMO and LUMO of both **2** and **8** are concentrated at the exocyclic double bond. Moreover, a detailed theoretical assessment of the reactions, especially for the diaryl derivatives available (see below), was not as straightforward in the late 1980s as now — experimentation was clearly necessary!



Scheme 11

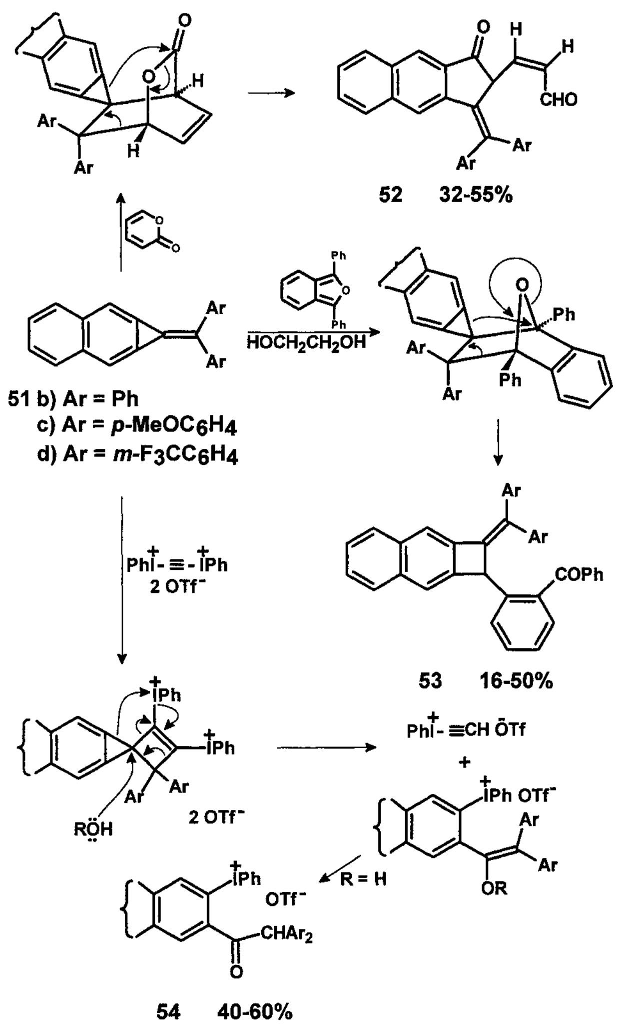


Scheme 12

Cycloaddition reactions proved to be difficult to bring about and much frustration was associated with the poor yields and long reaction periods needed. However, persistent efforts had their reward and with ethylene glycol as the solvent[97] yields improved and reaction times became shorter. For the cyclopropanaphthalenes **51b-d** the simplistic analysis bore fruit[98] as products **52** and **53** were formed (Scheme 13).

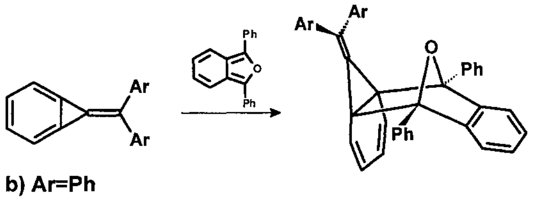
In our view each of these arises from an addition to the exocyclic π bond to give a spirocyclic [4+2] product that does not survive because of a facile path which provides for relief of ring strain. Furthermore, [2+2] cycloaddition with the highly electron deficient acetylenic(phenyl)iodonium triflates are also successful and lead, via ring expansion, to an ethanone as illustrated for **54** (Scheme 13). With diphenylisobenzofuran (DPIBF) the lower cyclopropabenzene homologues **50b** and **c** each give a single adduct.[99] Mass spectral analyses confirmed the products as 1:1 adducts, but the ^{13}C NMR spectra did not display the resonances expected at *ca.* 110-115 ppm for C2/5 cycloproparenyl carbons; cycloaddition could not have given a stable spirocycle from involvement of the exocyclic double bond. Despite full spectroscopic characterization the nature of the products was not clear and final structure solution was dependent on the good will of Boese and his colleagues in Essen. Indeed, a sample of the product from **50b** traversed a journey half way round the world, was subjected to x-ray data collection, the structure solved and the result transmitted by facsimile, all within a ten day period! And the result — cycloaddition occurs at the bridge bond of **50b** to give the Diels-Alder adduct **55** resulting from classical *endo* addition (Scheme 14).

Subsequent theoretical examination at the PM3 level[66,100] (to cope with the large substituents) showed that the addition of DPIBF to the exocyclic double bond of (unknown) **8** is 12 kcal mol^{-1} *more* exothermic than to the bridge bond. For (unknown) **2** the preference is for the bridge bond, again as observed for the substituted derivatives studied, but only



Scheme 13

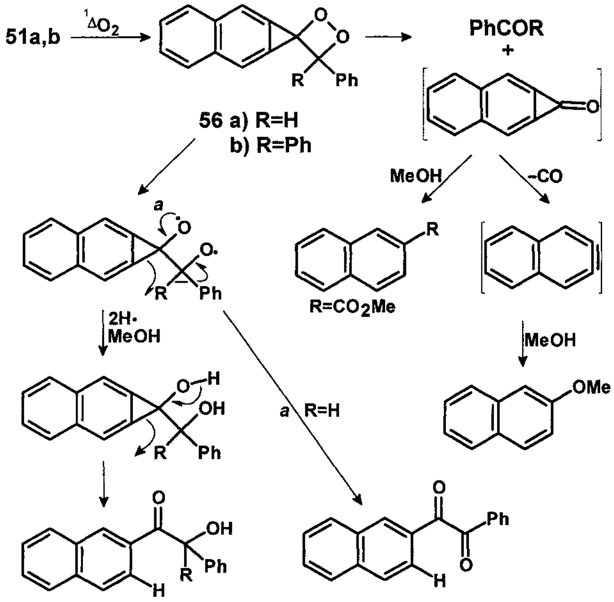
by 1.6 kcal mol^{-1} (-20.6 *vs* -19.0 kcal mol^{-1}, respectively). In fact, cycloaddition across the exocyclic double bond of **2** and **8** is exothermic to about the same extent (-19.0 and -20.9 kcal mol^{-1}, respectively), but addition to the bridge bond is far more exothermic for **2** than for **8** ($\Delta\Delta E$ -11.8 kcal mol^{-1}). More recent *ab initio* calculations[66] at the MP2/6-31G(d)//HF/6-31G(d) level suggest that in the addition of furan *both* **2** and **8** should favor the exocyclic bond by some 12-14 kcal mol^{-1}. However, the most recent PM3 results[66] are for the actual experimental study undertaken, *viz.* reactions of **50b** and **51b** with DPIBF, and they favor *endo* addition to the bridge bond in both cases with a preference of *ca.* 2 kcal mol^{-1} over the *exo* isomer. It seems likely, therefore, that the substituents present and the solvation effects in force are of paramount importance in determining which of the three possible pathways is actually followed.



Scheme 14

As yet there have been no studies on [2+2] reactions employing methylidenecyclopropabenzene derivatives, nor has any such reaction been the subject of computational study.

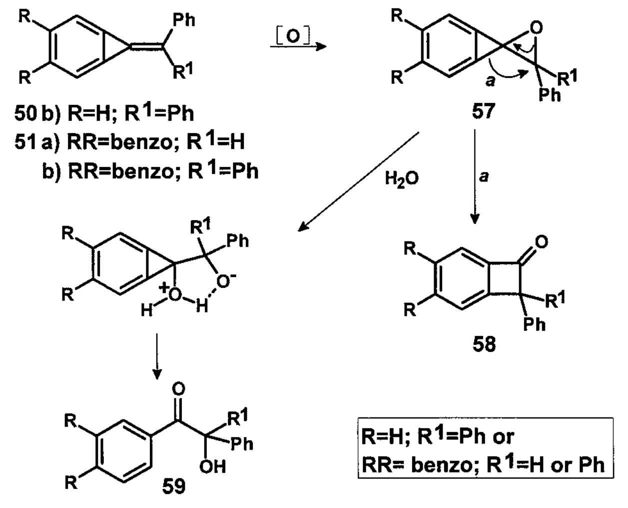
In addition to the reactions described above, the naphthalenes **51a** and **b** add singlet oxygen across the exocyclic π bond but the essential dioxetane intermediates, the novel dioxaspirohexenes **56** (Scheme 15), elude detection under the routine laboratory conditions employed.



Scheme 15

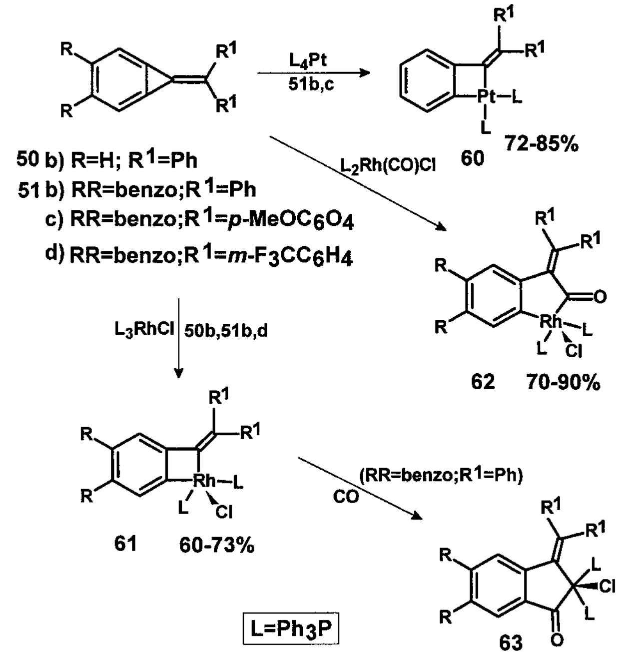
However, the plethora of products that are formed are readily accounted for[89] from these intermediates as shown in Scheme 15. In contrast, the benzenoid **50b** gives a largely inseparable mixture of products under the same conditions[89,101] and the involvement of the dioxetane analogue, while likely, cannot be assumed. If instead of singlet oxygenation, oxygen atom transfer is effected to the exocyclic olefin then the novel epoxide **57** should result thereby providing the first example of the highly strained oxaspiropentene framework. From use of peracid[89] the derivatives **50b** and **51a,b** provide the ethanones **59** that were plausibly proposed to result from **57** as the key reaction intermediate (Scheme 16) some years ago.[89] Much more recently we found[102] that, at ambient temperature, use of dimethyldioxirane under anhydrous aprotic conditions gave rise to a different product with **51b**, namely the cyclobutarenone **58** — epoxide **57** (RR=benzo; R^1=Ph) is again the likely intermediate. Conclusive proof came from use of deuterium labelled dimethyldioxirane in d_6-DMSO in the probe of an NMR instrument. At low temperature oxygen transfer is effected and ^{1}H and ^{13}C NMR spectra showed that **57** (RR=benzo; R^1=Ph) is produced. To our great delight the ^{13}C NMR spectrum of this spirocyclic cycloproparene and its precursor olefin were beautifully distinct and over a period of hours the substrate completely disappeared to leave the oxaspiropentene.[102] At -5°C thermal rearrangement of **57** (RR=benzo; R^1=Ph) into **58** is slow, but on warming to ambient temperature the resonances of the epoxide were replaced by those of **58** (Scheme 16) and the ketone was subsequently isolated in excellent yield. But all is not that straightforward as the attempted addition of methylene (from diiodomethane/diethylzinc) and chloromethylcarbene to **51b** have so far failed to afford characterizable materials.

The interaction of the methylidenecycloproparenes with organometallic reagents could provide interesting structures but few reaction have been studied so far. Those that have been assessed have involved the Group IX and X elements rhodium and platinum only.[31] The reactions show that it is the strained σ bond of the three-membered ring that is attacked and ring opening affords a metalacycle. Thus the diarylnaphthalene derivatives **51b** and **c** interact with tetrakis(triphenylphosphane)platinum(0) to give the platinacyclobutarenes **60**, while reactions of **50b** and **51b,d** with chlorotris(triphenylphosphane)rhodium(I) lead to the analogous rhodacyclobutarenes **61** (Scheme 17). The compounds are formed in very good yield, are crystalline and air-stable, and x-ray analysis of the bis(trifluoromethylphenyl)rhodium compound has been performed.[31] When one phosphane ligand of the rhodium substrate is replaced by CO, the oxidative addition of the metal is followed by



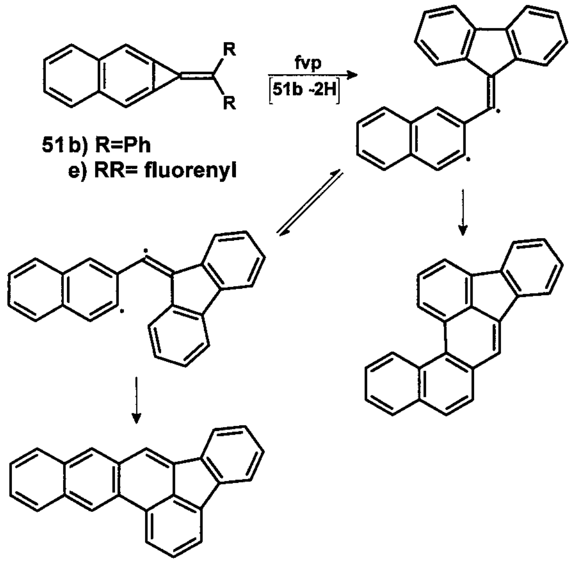
Scheme 16

migratory insertion of the carbon monoxide ligand to give the rhoda-3-alkylidenindan-2-ones **62** as established from crystal structure determination of the derivative from **51b**. When the rhodacyclobutarene **61** (RR=benzo; R^1=Ph) is treated with carbon monoxide insertion occurs to give the isomeric indan-1-one **63** as the major product.[31] This regiochemistry is dependent on the temperature employed and the preferential formation of **63** at low temperatures is nicely consistent with insertion into the weaker of the two rhodium-carbon bonds. While the chromium-complexed methylidenecyclopropanaphthalene **30** has been synthesised,[47] it was obtained from the metal-complexed disilyl and not by complexation of the preformed methylidene derivative **51b**.



Scheme 17

We noted at the beginning of this Section that the methylidenecycloproparenes have surprising thermal stability. This is not to say that thermal degradation cannot be induced, nor that more controlled rearrangement under *e.g.* fvp conditions cannot be achieved. To date only a preliminary skirmish with pyrolytic processes has been made.[103] The diphenylmethylidene **51b** and fluorenylidene **51e** were found to provide comparable pyrolysates that contained a good number of components, but the dibenzoacephenanthrylenes depicted in Scheme 18 are the only compounds so far isolated. Even from this restricted study it is clear that the aryl-substituted methylidenecycloproparenes have the potential to provide a range of polycyclic aromatics.



Scheme 18

5. Future Prospects

This survey of some of our recent chemical exploits has provided the highs and lows of several years study of methylidenecycloproparene chemistry in our laboratories. Not all of our work has followed a logical order (some would claim there never was any!) thereby leaving notable gaps in the knowledge base. As a consequence, it is hoped that these can be filled by *e.g.* applying the modified carbonyl addition-elimination sequence of synthesis to the methylidene cyclopropabenzene series, conducting a more complete and rigorous survey of electrophilic reactions, and providing a more meaningful assay of reactions with transition metal complexes. The cycloaddition chemistry offers encouragement for extension with heterodienes and dipolar species while the fvp studies clearly need to be repeated and extended.

The physicochemical properties of the compounds have shown them to be distinctly polar but as yet there are no measurements that have addressed the strength of the exocyclic double bond and the ease by which it might undergo rotation. The polar nature and exceptional fluorescence characteristics of certain members of the series argues for new derivatives that are functionalized in the cycloproparenyl component of the molecules to give extended push-pull compounds. The area thus offers encouragement because of possible future application of some of the molecules as laser dyes and others as new organic materials. Of course even more fascinating novel target molecules exist and we hope that future studies will provide for as much new and novel chemistry as has already emerged.

Acknowledgements.

The successes and failures recorded in this Account have come from the efforts of a small group of co-workers both in Salt Lake City and Wellington and they are named in the literature citations. Their intellectual input, genuine dedication and sheer good humor has made our involvement that much more enjoyable. Their efforts would have been impossible without continuing financial support. In Utah this is from the National Science Foundation and in Wellington from Victoria University, the NZ-US Educational Foundation (Fulbright Program) and the Claude McCarthy Trust. Our collaborations with Yitzhak Apeloig (Technion) and Roland Boese (Essen) and their groups have added perspectives to the programme that have markedly influenced progress in the area. We are grateful to them all in more ways than they will ever realise.

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