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Alkylidenecycloproparenes and Related Compounds

BRIAN HALTON*

Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand

PETER J. STANG*

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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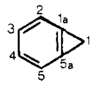
Strained ring systems are generally reactive and unstable[1] whereas molecules that satisfy the criteria for aromaticity have enhanced stability. The lower members of the ortho-bridged series of aromatic compounds combine both of these features into a single molecule and for this reason are an intriguing class of organic compounds. The parent member of the family, benzyne (**1**), is easily generated as a transient intermediate[2] which can be observed[3] spectroscopically in an argon matrix at 8 K. The next homologue, cyclopropabenzene[4] (**2**), is a remarkably stable and isolable compound[5,6] with a strain energy of 68 kcal/mol associated with the novel fused-ring system.[7] Cross-conjugated molecules such as the fulvenes, e.g. **3**, and the radialenes, e.g. **4**, are examples of another alluring class of strained molecules.[1] Whereas stable derivatives of the smallest fulvalene, methylenecyclopropene (**3**), have been known for almost 25 years,[8,9] **3** itself has only recently been reported[10] and is unstable at temperatures above −75 °C. Likewise the smallest parent radialene, trimethylenecyclopropane (**4**), polymerizes above 0 °C.[11]


1



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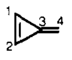

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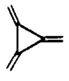
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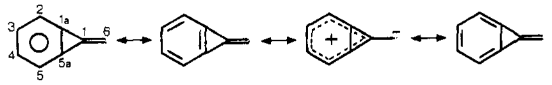
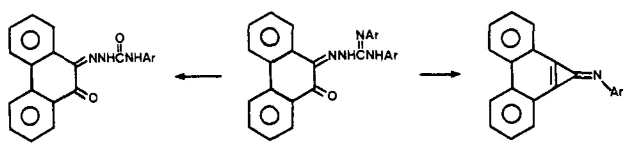


5 **5a** **5b** **5c**

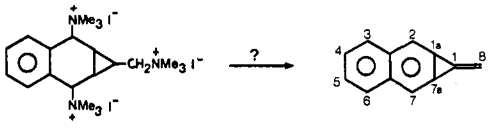
The alkylidenecycloproparenes, e.g. **5**, combine into one molecule the structural features associated with **2**, **3**, and **4**. Thus, **5** may be regarded as an ortho-fused cycloproparene, an exocyclic benzannulated **3**, a benzannulated triafulvene **5a–5b**, and an unusual radialene **5c**, all in one. In this Account we discuss the recent developments in alkylidenecycloproparene chemistry which includes some of the important chemical and physical properties. Relevant background on the related cycloproparenes is available in review form.[5]

Synthesis

While cyclopropabenzene was first mentioned in the literature 100 years ago,[12] the first claim[13] to the synthesis of such a compound was for the imines **7**, formed by decomposition of the iminosemicarbazones **6** of 9,10-phenanthroquinone. However, the report has proved to be nonreproducible,[14] with the semicarbazones **8** being the sole isolable products of reaction. More recently the triamine salt **9** was prepared[15] specifically as a precursor to methylenecyclopropa[*b*]naphthalene (**10**) but, to the best of our knowledge, the outcome of the necessary Hofmann eliminations has not yet been recorded. Even more recently it has been



8 **6** **7**



9 **10**

Brian Halton was born in England and graduated with a B.Sc. (hons.) and Ph.D. from the University of Southampton and, more recently, with a D.Sc. from Victoria University. After postdoctoral experience at the University of Florida, he moved to Victoria University in 1968 where he now holds the position of Reader in Chemistry. He was a Fulbright Scholar and Visiting Professor at the University of Utah in 1981–1982 and is immediate past-President of the New Zealand Institute of Chemistry. His research interests are strained organic molecules, photochemistry, and reaction mechanisms.

Peter J. Stang has been at Utah since 1969 where he is currently Professor of Chemistry. Recently, he was a Fulbright (Zagreb, Yugoslavia, 1987/1988), Lady Davis (Technion, Israel, 1986), JSPS (Kyushu, Japan, 1985), and David P. Gardner (Utah, 1984) Fellow. He is an Associate Editor for the *Journal of the American Chemical Society* and a member of the Editorial Advisory Board of *Synthesis*. His current research interests include alkynyl ester and alkynyliodonium chemistry, organometallic chemistry, strained ring systems, and unsaturated reactive intermediates.

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(1) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(2) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967.

(3) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134–6135.

(4) Fusion nomenclature requires that cyclopropabenzene (**2**) be named as bicyclo[4.1.0]hepta-1,3,5-triene.

(5) For reviews see: Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349–364. Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245–251. Halton, B. *Chem. Rev.* **1973**, *73*, 113–126.

(6) Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625–3631.

(7) 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.* **1978**, *95*, 7878–7880.

(8) Kende, A. S. *J. Am. Chem. Soc.* **1963**, *85*, 1882–1884. Battiste, M. A. *Ibid.* **1964**, *86*, 942–944.

(9) For a review see: Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1–109.

(10) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3693–3699. Staley, S. W.; Norden, T. D. *Ibid.* **1984**, *106*, 3699–3700.

(11) Dorko, E. A. *J. Am. Chem. Soc.* **1965**, *87*, 5518–5555.

(12) Perkin, W. H. *J. Chem. Soc.* **1888**, 1–20.

(13) De, S. C.; Dutt, D. N. *J. Indian Chem. Soc.* **1930**, *7*, 537–544.

(14) Halton, B.; Harrison, S. A. R.; Spangler, C. W. *Aust. J. Chem.* **1975**, *28*, 681–685.

(15) D'yakonov, I. A.; Mandel'shtam, T. V.; Kharicheva, É. M. *Zh. Org. Khim.* **1970**, *6*, 2252–2257 (*Chem. Abstr.* **1971**, *74*, 42213).

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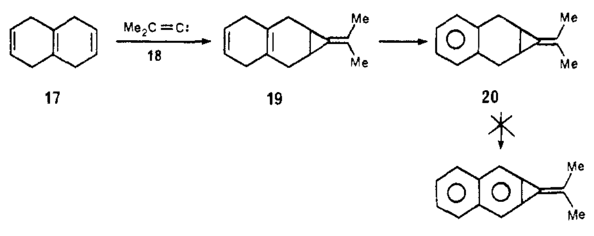
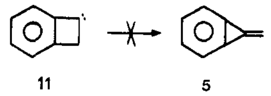
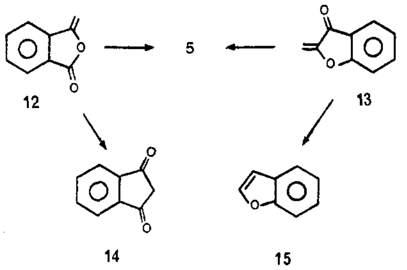
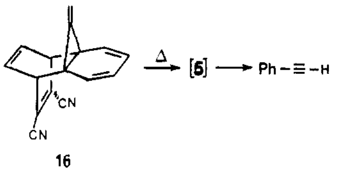
Scheme I



shown that ring contraction of cyclobutabenzenylidene (**11**) to methylenecyclopropabenzene (**5**) does not occur.[16] Moreover, flash vacuum pyrolysis of either **12** or **13** does not lead to the extrusion of carbon dioxide and formation of **5**;[17] **12** is stable to 900 °C and then rearranges to 1,3-indandione (**14**), while **13** loses carbon monoxide at 900 °C to give benzofuran (**15**). It has been found[18] that pyrolysis of **16** gives rise to phenylacetylene and *o*-dicyanobenzene. It seems clear that the Alder–Rickert cleavage of **16** provides parent **5** which rearranges to alkyne under the reaction conditions.



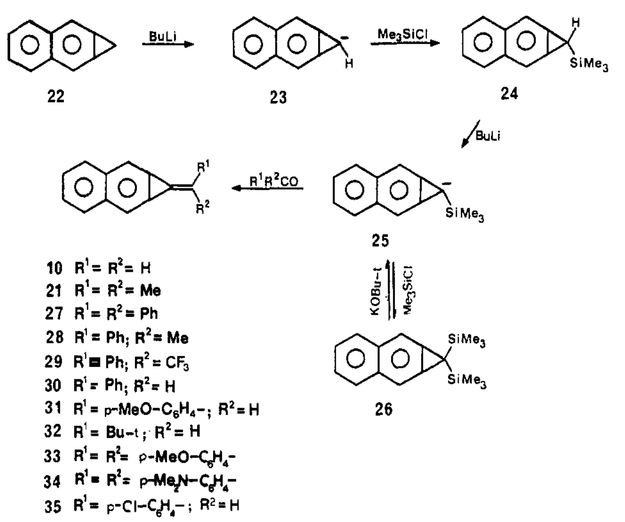




Since strained derivatives of naphthalene are known[1] to be more stable than those of benzene, and since alkyl or aryl substituents stabilize double bonds, our own initial attempts at the synthesis of an alkylidenecycloproparene were directed toward the preparation of **21** via the seemingly simple, logical two-step process outlined in Scheme I. Addition of the carbene[19] **18** to isotetralin (**17**) is known[20] to give the adduct **19** in reasonable yield. However, attempted oxidation of **19** with numerous reagents under a variety of conditions failed to provide the sought-after **21**; unchanged starting material, the partially oxidized benzobicycloheptane **20**, and polymers were obtained.

An alternative approach to the alkylidenecycloproparenes commences with a preformed ring system and is based upon the known[21] acidity of the benzylic protons of **2**. Thus metalation of **2** with butyllithium provides the cyclopropabenzenyl anion which can be captured with chlorotrimethylsilane. This, coupled with the facility of silicon to stabilize an α-anion[22] and the synthetic utility of the Peterson olefination[22,23] suggested to us that the title compounds might be available by the route depicted in Scheme II. This has proved to be the case[24] and the range[25,26] of cyclopropa[*b*]naphthalene derivatives **27**–**35** is now available in yields ranging from 10 to 98%.

Scheme II



Although successful the reaction sequence (Scheme II) is not as straightforward as might be implied. Treatment of cyclopropa[*b*]naphthalene[27] (**22**) with butyllithium and chlorotrimethylsilane gives the bis(silyl) derivative **26** and not **24**. Even with a carefully controlled addition of the base (1 M equiv) and the chlorosilane, bis(silyl) **26** is obtained in 47% yield and unchanged **22** (39%) is recovered. Because of the stabilization available to carbanion **25** by the adjacent silicon atom, it seems likely[25] that **24** is deprotonated immediately upon formation by residual **23** to give **25** and simultaneously regenerate **22** (Scheme II); mono(silyl) **24** has yet to be isolated. This is of little consequence since the removal of a trimethylsilyl moiety with *tert*-butoxide under anhydrous conditions is well documented[22,28] and **22** acts as a viable progenitor for **27**–**35**. Apart from the *tert*-butyl derivative **32** (which is an air-sensitive solid) compounds **27**–**35** are stable crystalline materials. The reaction sequence works best for benzophenone and its derivatives. With enolizable ketones anion **25** shows competition between silyl Wittig olefination and enolate ion formation. With acetophenone such competition restricts the yield of **28** to 42% whereas with acetone the olefination reaction

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(16) O'Leary, M.; Wege, D. *Tetrahedron Lett.* **1978**, 2811–2814. Dürr, H.; Nickels, H.; Philippi, W. *Ibid.* **1978**, 4387–4390.

(17) Bloch, R.; Orvane, P. *Tetrahedron Lett.* **1981**, *22*, 3597–3600.

(18) Klärner, F.-G.; Dogan, B. M. J.; Weider, R.; Ginsburg, D.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 346–348.

(19) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348–354, Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405.

(20) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 6461–6464.

(21) Eaborn, C.; Eidenschink, R.; Harris, S. J.; Walton, D. R. M. *J. Organomet. Chem.* **1977**, *124*, C27–C29. Eaborn, C. *Ibid.* **1980**, *192*, 155–161.

(22) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983.

(23) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784. Ager, D. J. *Synthesis*, **1984**, 384–398.

(24) Halton, B.; Randall, C. J.; Stang, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 6108–6110.

(25) Halton, B.; Randall, C. J.; Gainsford, G. J.; Stang, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 5949–5956.

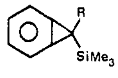
(26) Halton, B.; Lu, Q., unpublished results, 1986–1987.

(27) Billups, W. E.; Chow, W. Y. *J. Am. Chem. Soc.* **1973**, *95*, 4099–4100. Browne, A. R.; Halton, B. *Tetrahedron* **1977**, *33*, 345–348.

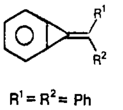
(28) Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153–160.

to give 21 is completely suppressed. The reaction between 25 and formaldehyde gives a complex mixture of products which does not appear to contain 10.[24,25]

Applied to parent 2,[29] these strategies lead to bis(silyl) 37 which is likewise converted[24] to alkylidenecyclopropabenzenes, e.g. 38. However, it has proved more practicable to effect the conversion of 2 into 38 by a direct procedure which bypasses 37 and avoids the necessity of having to isolate the known[21] monosilylcycloproparene 36. In this way the alkylidenecyclopropabenzenes 38–41 are available[25] in yields ranging from 10 to 40%. The lower yields recorded, compared to those for their higher homologues, 10, are explicable in part by a greater sensitivity to chromatographic separation and a lower thermal stability of these compounds.

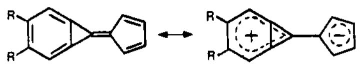


36 R = H
37 R = Me_3Si

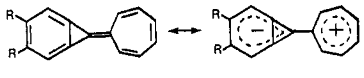


38 $R^1=R^2=$ Ph
39 $R^1=$ Ph; $R^2=$ Me
40 $R^1=$ Ph; $R^2=$ H
41 $R^1=$ p-MeO-C_6H_4- ; $R^2=$ H

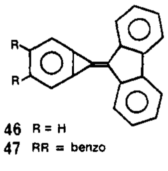
The potential triafulvene character 5a ↔ 5b associated with the alkylidenecycloproparenes has led to further exploitation[30] of the Peterson olefination of 2 and 22. A consideration of the cyclopentadienylidene homologues 42 and 43 shows that charge separation should be enhanced compared with 5b because of the presence of the "electron sink". In like manner the electron-donating ability of the cycloheptatrienylidene moiety, coupled with the stability of the cyclopropabenzenyl anion,[21,25] could neutralize or even reverse such polarity in fulvalenes 44 and 45. The cycloproparenylidene substructure in the fulvalenes is thus of particular interest as an ambiphile capable of stabilizing both positive and negative charge. Peterson olefination of 2 and 22 employing fluorenone gives the novel calicenes 46 and 47 in yields of 22% and 96%, respectively,[30] but the facile dimerization of cyclopentadienone prevents preparation of the parent compounds 42 and 43. In like manner, benzo[*d*]- and dibenzo[*b,f*]tropone have led to 48–51 as the first examples of triaheptafulvalenes. Although tropone itself is readily available reactions with it have not yet provided 44 and 45.



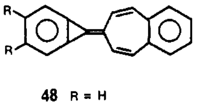
42 R = H
43 RR = benzo



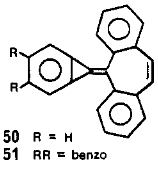
44 R = H
45 RR = benzo



46 R = H
47 RR = benzo

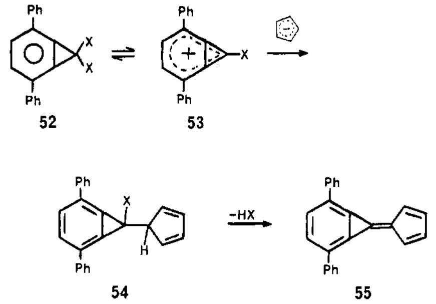


48 R = H
49 RR = benzo

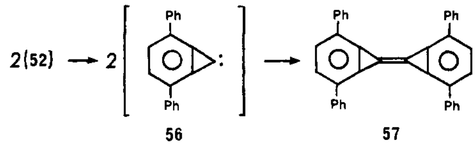


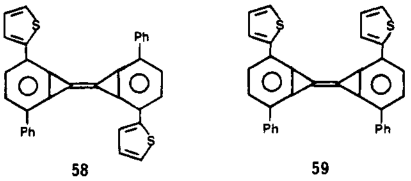
50 R = H
51 RR = benzo

Scheme III



A complementary approach to benzotriapentafulvalenes, e.g. 42, has employed the cyclopropabenzenyl cation as a synthon (Scheme III). The readily available[31] *gem*-dihalocyclopropabenzene 52 ionizes[32] to cation 53. Coupling of 53 with the cyclopentadienyl anion is expected to afford 54 which should eliminate HCl easily to give benzocalicene 55. Although this pathway has direct analogy with the synthesis of many calicenes,[33,34] all attempts to bring the sequence to fruition have failed.[35] However, it has now been found[36] that the reaction of 52 with base (BuLi) leads to the dibenzotriafulvalene 57 via the cyclopropabenzenylidene 56. By commencing with an unsymmetrical cycloproparene, Neidlein[36] has obtained the *E*/*Z* isomers 58 and 59 in a 1:1 ratio. Compounds 57–59 are the first examples of the cyclopropenylidene or triafulvalene class of compounds the parent member of which is a structural isomer of benzyne (1).





58 59

Structure and Spectroscopy

The available alkylidenecycloproparenes are colored crystalline solids and, with the exception of 32, these provide the first examples of stable hydrocarbons which contain the methylenecyclopropene/trimethylenecyclopropane moieties. Of fundamental importance in any study of these compounds is the nature of the bonding and the presence or absence of charge separation, cf. 5a–c. The available range of derivatives has allowed for the measurement of several useful physicochemical parameters which serve to address these questions.

The expectation[9] of polarity in the alkylidenecycloproparenes, and in particular in the fulvalenes 42–51,

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(29) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. *Org. Synth.* **1976**, *55*, 12–15.

(30) Halton, B.; Buckland, S. J.; Mei, Q.; Stang, P. J. *Tetrahedron Lett.* **1986**, *27*, 5159–5160.

(31) Halton, B.; Milsom, P. J.; Woolhouse, A. D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 731–735.

(32) Halton, B.; Hugel, H. M.; Kelly, D. P.; Müller, P.; Burger, U. *J. Chem. Soc., Perkin Trans. 2* **1976**, 253–263.

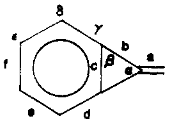
(33) Prinzbach, H.; Fischer, U. *Helv. Chim. Acta* **1967**, *50*, 1667–1691, 1692–1722. Bergmann, E. D.; Agranat, I. *J. Chem. Soc., Chem. Commun.* **1965**, 512–513.

(34) Yoshida, Z.; Araki, S.; Ogoshi, H. *Tetrahedron Lett.* **1975**, 19–22.

(35) Halton, B.; Russell, S. G. G., unpublished observations, 1986.

(36) Neidlein, R.; Poignée, V.; Kramer, W.; Glück, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 731–732.

Table I.
Selected Bond Distances (Å) and Interbond Angles (deg) for Cyclopropabenzene (2), 1-Diphenylmethylene-1*H*-cyclopropabenzene (38), and Methylenecyclopropene (3)



	a	b	c	d	e	f	α	β	γ	δ	ϵ
2[a]		1.498 (3)[d]	1.334 (4)	1.363 (3)	1.387 (4)	1.390 (5)	52.9 (2)	63.6 (1)	124.5 (2)	113.2 (2)	122.4 (2)
38[b]	1.343 (4)	1.433 (5)	1.355 (4)	1.379 (5)	1.384 (6)	1.388 (6)	56.4 (2)	61.8 (3)	123.9 (4)	113.0 (4)	123.0 (4)
3[c]	1.332 (6)	1.441 (6)	1.323 (3)				54.7 (5)				

[a] Data provided by Dr. Boese; see ref 44. [b] Data taken from ref 25. [c] Data taken from ref 39. [d] Error in last digit.

is supported by ab initio molecular orbital calculations. Although **2** is expected to have a negligible dipole (calculated value, 0.07 D),[37] **5** should have polarity as depicted by **5b** with a dipole moment of 1.49 D.[38] This compares well with that calculated and measured[39] for **3** as 1.90 D since the benzo fusion in **5** should moderate the effect. By comparison, the calculated[38] dipole moment of benzocalicene is 3.28 D in the direction indicated in **42** and that measured[30] for **46** is 2.6 D, whereas the value[26] for **38** is 1.0 D. Thus the presence of the cyclopentadienyl "electron sink" plays its expected role in enhancing the polarity. Ambiphilicity associated with the cycloproparenyl moiety, **42** vs **44**, might seem established[30] since the dipole moment of **50** is measured as 1.2 D. The calculated value for **44** (1.12 D) agrees well, *but the direction is the opposite to that depicted*; the positive end of the dipole is the cycloproparenyl moiety and the cycloheptatrienyl unit is relatively negative![38] The polarity of **3** has been explained[39] in terms of a two-electron π-stabilizing donation from the C_1–C_2 π-bond to the C_3–C_4 π-bond that accouts for about 37% of the negative charge of C_4 while four-electron polarization of the C_3–C_4 bond accounts for 63% of this charge. The effect of this is for the dipolar character, with negative charge at C4, to contribute about 20% to the ground state of **3**. It seems likely that the same effects operate in **5** and are perhaps more obvious in **44** and **50**.

The alkylidenecycloproparenes show infrared absorptions which can be regarded as characteristic.[25] Thus absorptions in the ranges 1765–1790 and 1510–1550 cm^{-1} compare with 1810–1880 and 1510–1550 cm^{-1} for derivatives of **3**[9] and with 1770 and 1519 cm^{-1} for **3** itself.[10] These bands probably result[9] from strong coupling between the exo- and endocyclic double bonds. Moreover, the shift in the higher energy transition to lower wavenumber is consistent with a dipolar structure. In the ultraviolet region, long wavelength absorptions (**38**, 381, 398; **27**, 412, 438; **46**, 411, 438 nm) account for the color of the compounds. More importantly, these maxima are shifted to shorter wavelengths by 5–7 nm when the medium is changed from nonpolar to polar. Although small, these hypsochromic shifts are in the opposite sense to those expected for $\pi \rightarrow \pi^*$ transitions with such a solvent change. Moreover, the shifts are uniformly larger for the fulvalenes, e.g. **46**, than the fulvenes, e.g. **38**. This negative solvatochromy is typical of other polar fulvalenes and fulvenes[33,40] and supports the presence of charge separation.

The presence of aromatic substituents at the exocyclic center of the stable alkylidenecycloproparenes masks the cycloproparenyl ^{1}H NMR resonances and prevents an analysis of the data. The ^{13}C NMR spectra display[25] signals for the quaternary exocyclic double bond carbons in the range 105–120 ppm, but the absence of suitable model compounds (aryltriafulvenes are unstable and data are lacking) does not allow conclusions to be drawn with regard to charge separation and bond localization. However, the retention of the cycloproparenyl ring system is evident from the characteristic[5] resonances of the shielded carbon atoms adjacent to the fused three-membered ring which appear in the range 105–115 ppm. In **3** the methylene carbon (C4) resonates at 59.6 ppm while C1 and C2 appear at 132.9 ppm. Together with the ^{1}H NMR data, the shielding of C4 in **3** is taken as support for significant charge separation in the molecule. Furthermore, it is interesting to note that C1(2) of **3** resonates at lower field than the ring sp^2 centers in 1,2-dimethylenecyclopropane (124.8 ppm),[41] but with comparable chemical shift to the C1a(5a) carbons of alkylidene derivatives **38**–**41**.

The concept of bond localization was introduced as long ago as 1930 by Mills and Nixon.[42] The argument is for a nonequivalence of the bonds in a benzene ring as a result of 1,2-ring fusion and this should manifest itself most in the strained cycloproparenes. The available structural data for derivatives of **2** show bond length and bond angle deformations from normal, but these can only be interpreted in terms of the fused ring system accommodating the imposed stress and strain; there is no evidence for bond fixation.[5,43]

Crystallographic parameters have been measured[25] for **38**, and the molecular structure of **3** is available from microwave studies.[39] Furthermore, parent **2** has been crystallized (mp −70 °C) and an X-ray structure determination performed[44] at −153 °C. The parameters determined from these studies are shown in Table I. The short bridge bond of **2** (1.334 Å) is reproduced exceptionally well by ab initio calculations (1.337 Å, 3-21G)[37] and it lies between those of **38** and **3** (bond c,

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(37) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1986**, *108*, 3241–3247.

(38) Apeloig, Y.; Arad, D., unpublished observations. We thank Professor Apeloig (Technion, Haifa) for providing us with his results prior to publication.

(39) Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912–7918.

(40) Prinzbach, H.; Knothe, L. *Pure Appl. Chem.* **1986**, *58*, 25–38. Prinzbach, H. *Ibid.* **1971**, *28*, 281–329. Neuenschwander, M. *Ibid.* **1986**, *58*, 55–66. Prinzbach, H.; Woischnik, E. *Helv. Chim. Acta* **1969**, *52*, 2472–2476.

(41) Belzner, J.; Szeimes, G. *Tetrahedron Lett.* **1986**, *27*, 5839–5842.

(42) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510–2524.

(43) Allen, F. H. *Acta Crystallogr., Sect. B* **1981**, *B37*, 900–906.

(44) Neidlein, R.; Christen, D.; Poignée, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Pêrez, C.; Hübner, T. *Angew. Chem., Int. Ed. Engl.*, in press. We thank Dr. Boese (University of Essen) for providing these data prior to publication.

Scheme IV

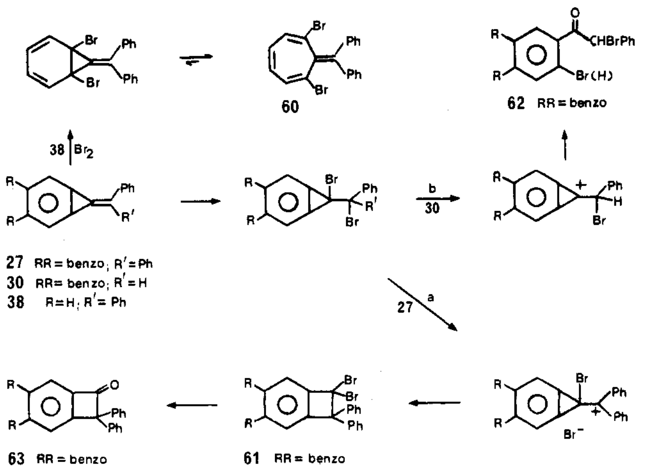


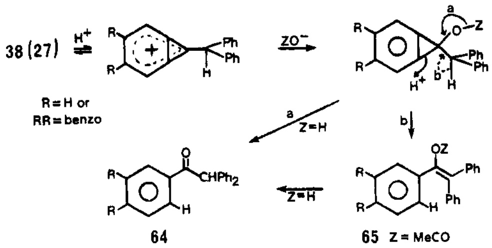
Table I), viz. the bridge bond of **38** is *longer* than those in **2** and **3**. By comparison, the σ-bond emanating from C1a and C5a (bond b) of **38** is significantly *shorter* than those of **2** but is comparable to those in **3**. The exocyclic double bonds of **3** and **38** are of comparable length and fall within the expected range. The remaining features associated with **38** parallel those present in **2** and other cycloproparenes.[5] Moreover, the interbond angles are comparable, save for α and β of **38** which reflect the change in the bond lengths of the three-membered ring. Thus the effect of the exocyclic double bond in **38** is small by comparison with **2** and no conclusions can be drawn with regard to the nature of **5**. Indeed, as Apeloig has noted,[37] it is important to recognize that the concept of bond fixation (and charge separation) is concerned with the localization of electrons in the π-framework while the molecular geometry is determined by both π- and σ-effects.

The highly distorted geometry displayed by **38** (and **2**), particularly about the sites of fusion of the three-membered ring, is expected to be common to the alkylidenecycloproparenes. The recorded and calculated dipole moments, and to some extent the spectral data, support a polar structure as depicted by **5b**, the extent of which is influenced by the nature of the substituents attached to the exocyclic double bond.

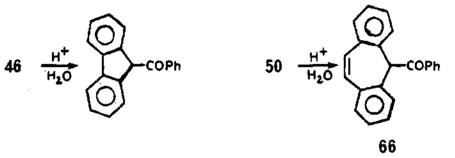
Chemical Properties

The chemistry of the alkylidenecycloproparenes is dominated by reactions which result in cleavage of the three-membered ring. For example, the reaction of **57** with Pd/C and hydrogen gives the corresponding 1,2-diarylethane at room temperature.[36] However, not all reactions result in a substituted benzene; **38** adds bromine across the bridge bond[5] to give heptafulvene **60** in modest yield.[45] By comparison, additional energy would be needed to lose aromaticity in homologue **27** and bromination leads instead to moisture-sensitive **61** by ring expansion (Scheme IV). Bromination of **30**, which has only one phenyl substituent on the exocyclic double bond, gives **62** on work-up. The difference in behavior between **27** and **30** reflects a delicate, but understandable, balance between diarylmethyl and cycloproparenyl cation formation as depicted by paths a and b of Scheme IV.

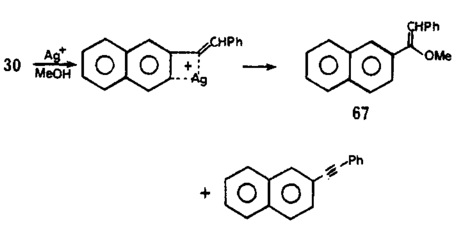
Scheme V



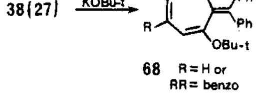
With other electrophiles reaction is dominated by capture of the electrophile at the exocyclic center and formation of a cycloproparenyl cation (Scheme V).[45] Subsequent reaction with the counterion is invariably accompanied by opening of the three-membered ring. Thus **38** (and **27**) gives ethanone **64** with aqueous acids while anhydrous acetic acid leads to the vinyl acetate **65**. Acid catalyzed ring opening of calicene **46** proceeds in a strictly analogous fashion, as expected in view of the polarity of the molecule, and 9-benzoylfluorene is formed.[35] Triaheptafulvalene **50** reacts[46] in precisely



the same way to give **66** and the formation of this product is consistent with the positive end of the dipole residing in the cycloproparenyl moiety as has been calculated (see above). Silver(I) catalyzed methanolyses afford[45] vinyl ethers, e.g. **67**, in direct analogy[5] with the cycloproparenes, but when the substrate carries a vinylic hydrogen atom, e.g. **30**, the corresponding diarylethyne is also formed.



The alkylidenecycloproparenes are generally resistant[46] to nucleophilic reagents. However, upon prolonged exposure (~140 h) to a large excess of *tert*-butoxide, ring expansion to a heptafulvene, e.g. **68**, ensues. It is presumed that nucleophilic addition to the strained bridge bond of the substrate gives the norcaradiene derivative which tautomerizes to product.



Oxidation of the exocyclic double bond of **5** and its derivatives is of particular interest since it could provide a viable pathway to the elusive and reactive[5] 1-oxocyclopropabenzene **71**. Derivatives of **71** exist as reactive molecules in solution,[47] and **71** itself has been

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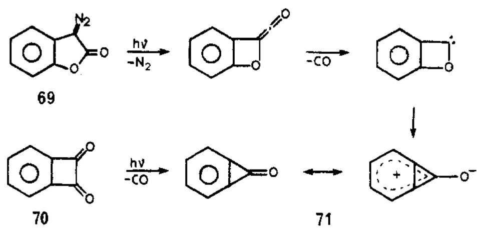
(45) Buckland, S. J.; Halton, B.; Mei, Q.; Stang, P. J. *Aust. J. Chem.* **1987**, *40*, 1375–1387.

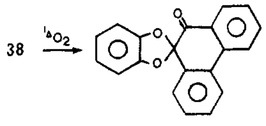
(46) Buckland, S. J.; Halton, B., unpublished observations, 1986–1987.

(47) Ao, M. S.; Burgess, E. M.; Schauer, A.; Taylor, E. A. *J. Chem. Soc., Chem. Commun.* **1969**, 220–221. Adamson, J.; Forster, D. L.; Gilchrist, T. L.; Rees, C. W. *Ibid.* **1969**, 221–222; *J. Chem. Soc. C* **1971**, 981–988.

Scheme VI

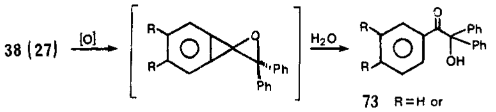


isolated[3,48] in a matrix at 8 K from photolysis of **69** and **70** (Scheme VI). While reaction of **27** with singlet oxygen gives benzophenone (20%), the isolation of methyl 2-naphthoate (25%) and 2-methoxynaphthalene (7%) confirms the intervention of 1-oxocyclopropa[*b*]naphthalene.[46] The benzene homologue **38** gives the unusual spirocycle **72** (identified by X-ray analysis[49]) in low (6%) yield. Analogous studies with inorganic



72

oxidizing agents, e.g. osmium tetroxide, have also failed[50] to provide **71**. With peracids α-hydroxy ketones **73** are formed[46] and it is presumed that these arise from epoxidation and the subsequent nucleophilic addition of water to the epoxide. However, the site of attack on the epoxide (C1 vs C6) is not known. Unlike the epoxidation sequence, there is no reaction of **27** with carbenes under a variety of conditions which include those known[51] to be effective for bicyclopropylidene.



73 R=H or RR=benzo

Electrochemical and spectroelectrochemical investigations[52] of **27** (and **38**[53]) have shown that a stable radical anion (λ_{max}: **27**, 519; **38**, 587 nm) and a quasi-stable radical cation can be formed. The reduction and oxidation steps are reversible, which implies retention of the ring system and formation of the corresponding radical anion **74** and radical cation **75**.

74 R=H or RR=benzo 75

Conclusion

Despite their recent availability the alkylidenecyclopropanes have obvious interest as the first, simple, stable, and polar hydrocarbons to contain a three-membered carbocycle with trigonal-planar hybridization at each center. The comparative ease of synthesis provides the potential for a wide range of derivatives and encourages alternative approaches to the as yet unknown parent hydrocarbon. Much of the chemistry of this intriguing class of compounds remains to be explored.

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(48) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586–6588.

(49) Buckland, S. J.; Gainsford, G. J.; Halton, B., unpublished observations, 1986.

(50) Mei, Q.; Stang, P. J., unpublished observations, 1986.

(51) Erden, J. *Synth. Commun.* **1986**, *16*, 117–121.

(52) Ashley, K.; Foley, J. K.; Mei, Q.; Ghoroghchian, J.; Sarfarazi, F.; Cassidy, J.; Halton, B.; Stang, P. J.; Pons, S. *J. Org. Chem.* **1986**, *51*, 2089–2092.

(53) Ashley, K.; Sarfarazi, F.; Buckland, S. J.; Foley, J. K.; Mei, Q.; Halton, B.; Stang, P. J.; Pons, S. *Can. J. Chem.*, **1987**, *65*, 2062–2068.

Paired Interacting Orbitals: A Way of Looking at Chemical Interactions

HIROSHI FUJIMOTO

Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan

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Introduction

Molecular orbital calculations provide us with useful information about the structures and the physical properties of organic and inorganic molecules.[1] For instance, it is possible to find the transition-state structure of a chemical reaction and trace the reaction path on the potential surface.[2] As theoretical calculations become more available and more reliable, it will be more important to have powerful methods for analyzing the results. It is helpful to know some of the factors that will control the stability of bonds and selectivity of reactions.

In fact, we already have a very useful way of generalizing the nature of chemical interactions and chemical bonds called the concept of "orbital interactions".[3-5]

Hiroshi Fujimoto was born in Kyoto, Japan, in 1938. He received a Ph.D. from Kyoto University where he is now an Associate Professor. His primary interests are in theoretical treatments of organic reactions and molecular interactions.

(1) See for example: *Applications of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum: New York, 1977.

(2) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161.

(3) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: West Berlin, 1975.

(4) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970.

0001-4842/87/0120-0448$01.50/0