Benzocyclopropenes

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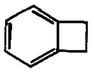
Contents

I. Introduction

Considerable attention has been given to the chemistry of small strained carbocyclic ring systems. Benzocyclopropene, which results from the fusion of cyclopropene to a benzene ring, is the parent and most highly strained member of the benzocycloalkene series. The isolation of benzocyclobutene (**1**), by Cava and Napier in 1956,[1] and the observation that dehydrobenzene (**3**) is a transient intermediate in many reactions,[2] led to the belief that benzocyclopropene (**2**), the missing middle member of the series, should at least be capable of transient existence.[3] The strain energy of benzocyclopropene has been estimated[3] to be at least 45.5 kcal mol^{-1} greater than that of cyclopropane, and it was not until 1964 that the first derivative of the ring system was isolated.[4]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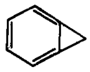
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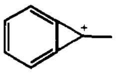
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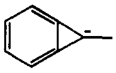
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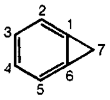
Apart from the obvious interest of the experimental chemist in the synthesis and properties of strained small ring systems, many such molecules have provided the theoretician with appropriate models for developing the concepts of chemical bonding and aromaticity. Benzocyclopropene is of such interest to the theoretical chemist.[5] The strain associated with the ring system should result in accommodation of the aromatic sextet with partial aromatic bond fixation and consequent bond length alternation in the aromatic ring. The derived benzocyclopropenyl cation (**4**) and anion (**5**) are of further interest with respect to electron delocalization and aromatic character.

Although the comprehensive review on cyclopropenes,[6] published by Closs in 1966, includes some aspects of benzocyclopropene chemistry, no prior review article on this subject has appeared. The purpose of the present review is to provide a survey of the literature on the methods of preparation of benzocyclopropenes, to discuss the theoretical implications of the ring system, and to compare the chemistry with that of the corresponding cyclopropenes; *Chemical Abstracts* has been reviewed through March 1972. There is some debate on the direction of aromatic bond fixation in benzocyclopropene (**2** *vs.* **6**),[5] but for the purpose of this review the π system and the numbering of the substituents will be represented as indicated in **2** even though it does not always agree with that used by the original authors.



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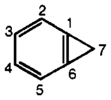

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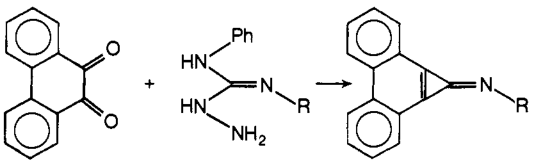
II. Synthesis of Benzocyclopropenes

A. Historical Approaches

The earliest report of a cyclopropene fused to an aromatic ring appeared in 1930. De and Dutt[7] claimed that a series of 1-aminodiarylguanidines condensed with 9,10-phenanthroquinone to give the corresponding phenanthro[*l*]cyclopropenone imines **7**. Evidence for the structure assignments rests on the analytical data of the products, and the report remains unsubstantiated. No further accounts of benzocyclopropene synthesis appeared until 1953 when Mustafa and Kamel examined the addition of diphenyldiazomethane to the quinone imides **8** and **10**.[8] The products obtained were nitrogen free and assigned as **9** and **11**, respectively (Scheme I). Reaction of **10** with 9-diazofluorene was likewise reported to give the spirobenzocyclopropene **12**. Considerable doubt must be



7

R = aryl

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(1) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **78**, 500 (1956); **80**, 2255 (1958). For a review see I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

(2) R. W. Hoffmann, "Dehydrobenzene," 2nd ed, Academic Press, London, 1967.

(3) E. F. Ullman and E. Buncel, *J. Amer. Chem. Soc.*, **85**, 2106 (1963).

(4) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).

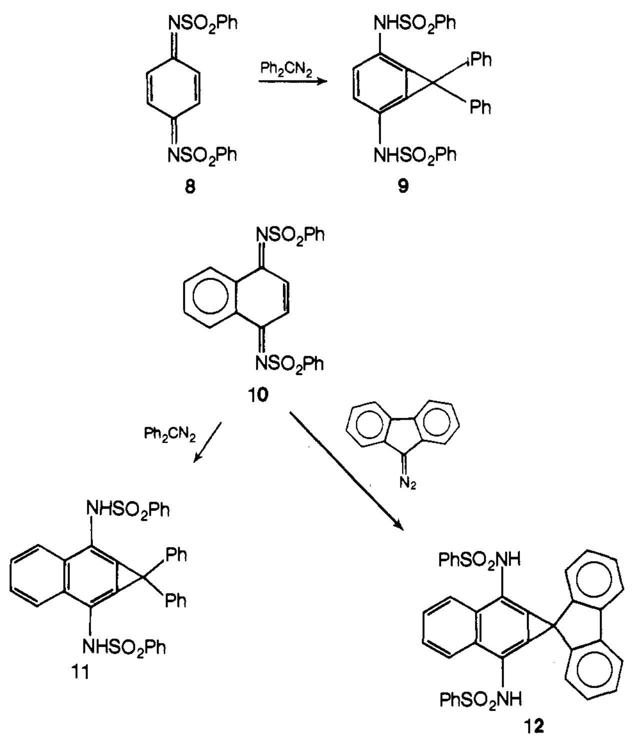
(5) C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 701 (1971).

(6) G. L. Closs, *Advan. Alicyclic Chem.*, 1, 53 (1966).

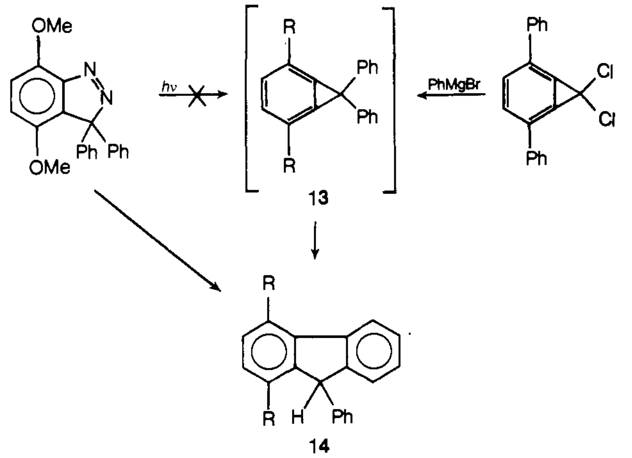
(7) S. C. De and D. N. Dutt, *J. Indian Chem. Soc.*, 7, 537 (1930).

(8) A. Mustafa and M. Kamel, *J. Amer. Chem. Soc.*, **75**, 2939 (1953).

SCHEME I

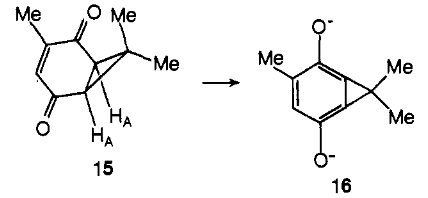


placed on the structures assigned to these products[9] since more recent attempts to obtain the 7,7-diphenylbenzocyclopropenes **13** have led to the isolation of the fluorene derivatives **14**.[10,11]

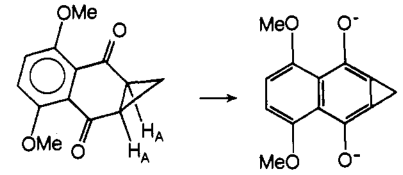


a, R = OMe; **b**, R = Ph

The first serious, though unsuccessful, attempt at the synthesis of a benzocyclopropene derivative was made by Ullman and Buncel in 1963. These authors[3] attempted to generate the dianions **16** and **18** by base abstraction of the cyclopropane bridge protons, H$_A$, of bicyclo-[4.1.0]hept-3-ene-2,5-dione **(15)** and the dimethoxybenz-substituted analog **17** respectively. Attempts to trap or detect the dianion failed, compound **15** decomposing under the reaction conditions. However, **17** underwent facile deuterium exchange of protons H$_A$ in CH$_3$ONa–CH$_3$OD or *t*-BuOK–*t*-BuOD, but it was shown that this exchange occurred exclusively from the monoanion.



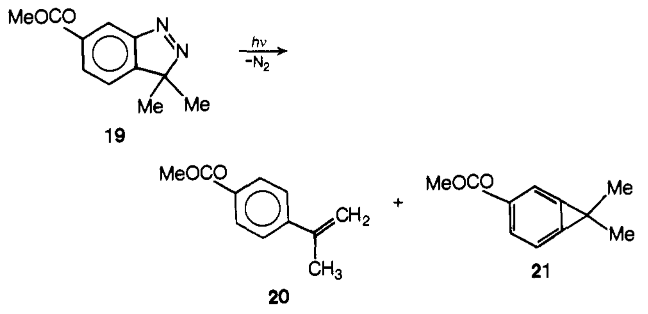
15 **16**



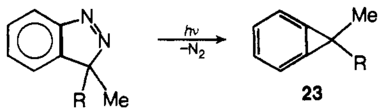
17 **18**

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

The first successful synthesis of a benzocyclopropene derivative was accomplished in 1964. Anet and Anet[4] found that photolysis of the 3*H*-indazole **19** led to the elimination of molecular nitrogen and the formation of methyl 7,7-dimethylbenzocyclopropene-3-carboxylate **(21)** in low yield. Methyl 4-isopropenylbenzoate **(20)** was the major reaction product.



The photolysis of 3*H*-indazole derivatives has been extended by Closs and coworkers,[12] and the method now constitutes an important route to geminal-disubstituted benzocyclopropenes. The reaction has been shown to proceed through a diradical intermediate and is clearly analogous to the synthesis of cyclopropenes from 3*H*-pyrazoles developed by this same group of workers.[13] Irradiation of the indazoles **22a–c** at 77°K in the cavity of an esr spectrometer gave spectra compatible only with triplet diradical species, and these data have been taken to suggest the presence of molecules with structure **25**.[12] Subsequent cyclization gives rise to the observed benzocyclopropene products. The geometry of **25** is probably planar, but the orientation of the substituents with respect to the ortho radical site is not known. Furthermore, it is not known whether **25** is produced directly from the indazole or in a two-step process involving the diazo compound **24**. Some support for the intervention of **24** comes



22 **23**

a, R = CO$_2$Me; **b**, R = MeO; **c**, R = CN

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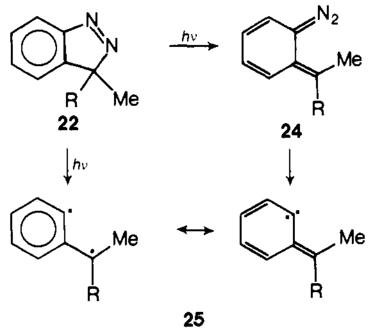
(9) A claim that the structures assigned by Mustafa and Kamel[8] are incorrect has been made, but the corrected structures have not yet been published; see ref 19, p 6.

(10) H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1467 (1968).

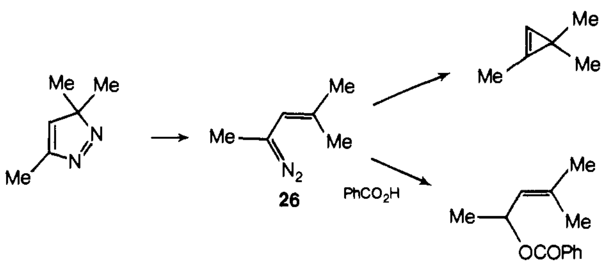
(11) B. Halton and P. J. Milsom, unpublished observations.

(12) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

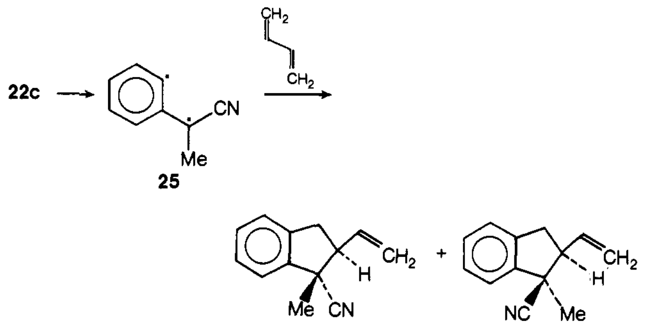
(13) G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 399 (1963); *J. Amer. Chem. Soc.*, **85**, 3904 (1963).



from the isolation of **26**, in 50% yield, from the irradiation of 3,3,5-trimethyl-3*H*-indazole in the absence of both visible light and ultraviolet radiation of wavelength less than 320 nm.[14]

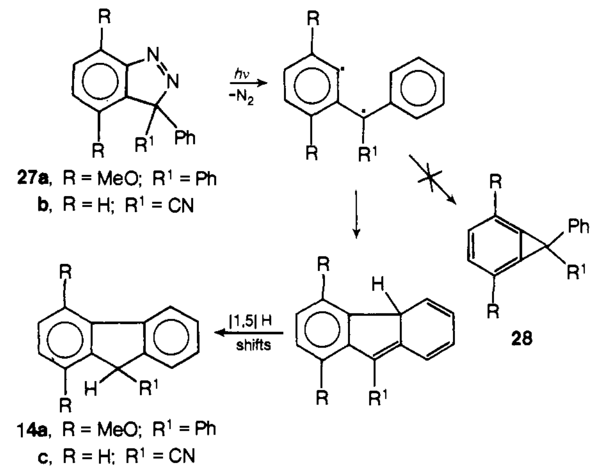


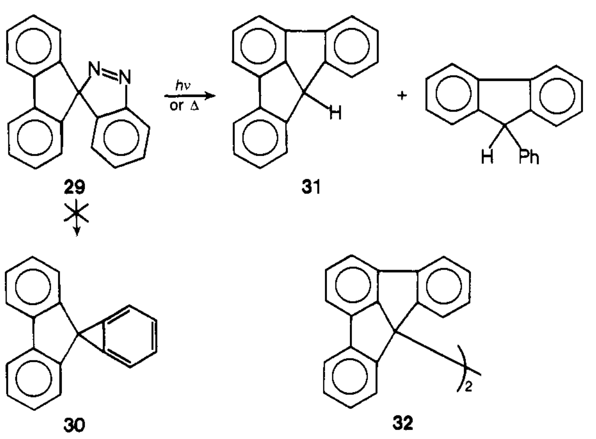
Chemical evidence for the diradical intermediate **25** has also been obtained from the low-temperature photolysis of **22c** in butadiene. Under these conditions isomeric indanes are obtained by the addition of **25** to the solvent.[12]



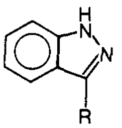
Attempts to extend the elimination reaction to the synthesis of the 7-substituted 7-phenylbenzocyclopropenes **28** have failed. Photolysis and thermolysis of 3-cyano-3-phenyl-3*H*-indazole (**27b**) lead only to 9-cyanofluorene (**14c**) in yields greater than 93%.[15] Similarly, **27a** gives the 9-phenylfluorene (**14a**) as the sole isolable product of reaction.[10] These processes can be rationalized as involving a triplet diradical which, with spin inversion, cyclizes at the ortho position of the phenyl substituent (Scheme II). The fluorene derivatives can then result from a series of thermally allowed [1,5] hydrogen shifts.[16] The formation of compounds **14** in this way parallels the production of indenes from the photochemical[17] and thermal[18] rearrangements of tetraarylcyclopropenes. The 3*H*-indazole route to benzocyclopropenes has also failed to yield the spiro derivative **30**.[15,19] Photolysis or thermolysis of the spiro-3*H*-indazole **29** gives rise to fluoradene (**31**), 12,12′-bifluoradene (**32**), and 9-phenylfluorene; the last product arises by hydrogen abstraction from the solvent and **31**. The fluoradene could arise by a mechanism analogous to that outlined above for the formation of **14**, but the diradical process would have to be much less caged to account for the formation of the products.

SCHEME II





A more serious limitation of the 3*H*-indazole synthesis of benzocyclopropenes is that the method is restricted to the synthesis of geminal disubstituted derivatives. This is because 3-monosubstituted indazoles exist only in the 1*H* tautomeric form **33**.



33

A novel synthesis of benzocyclopropenes, involving 3*H*-indazoles as intermediates, has been achieved by Dürr and Schrader.[20] Photoelimination of nitrogen from the spiro-3*H*-pyrazoles **34** did not give rise to spirocyclopropene products as anticipated,[21] but, instead, led to the benzocyclopropenes **35**. The mechanism proposed for the reaction (Scheme III) involves initial ring expansion to the indazoles **36** which then lose nitrogen to give the observed products as discussed above. The ring enlargement step is

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(14) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968).

(15) G. Baum, R. Bernard, and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5307 (1967).

(16) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

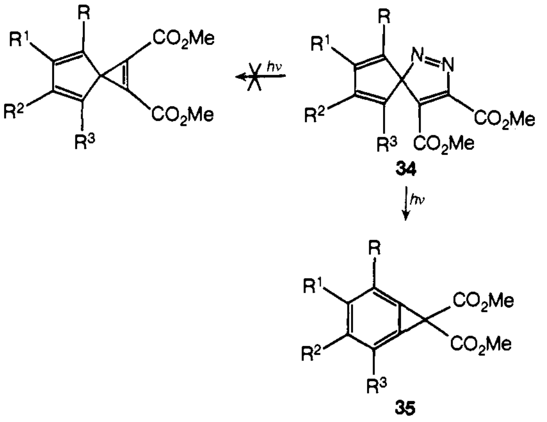
(17) B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971).

(18) (a) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967); (b) R. H. Grubbs, M. S. Thesis, University of Florida, 1965.

(19) G. Baum, Ph.D. Thesis, The Ohio State University, 1965.

(20) H. Dürr and L. Schrader, *Angew. Chem.*, **81**, 426 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 446 (1969); *Chem. Ber.*, **103**, 1334 (1970).

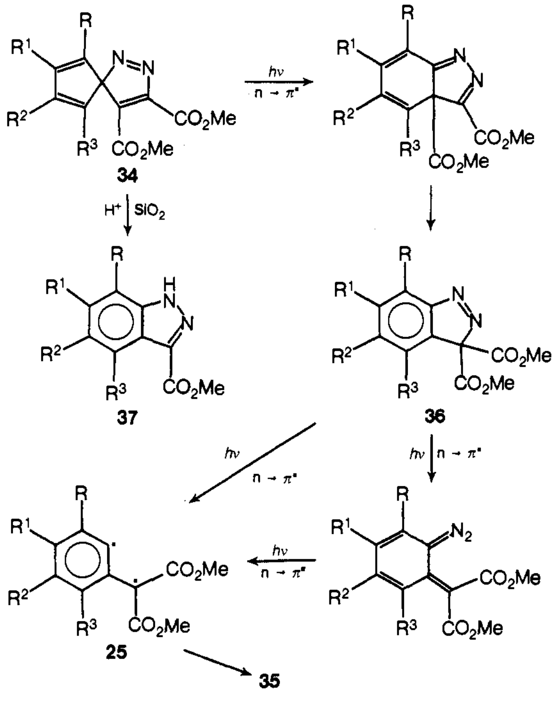
(21) (a) G. Ege, *Tetrahedron Lett.*, 1667 (1963); (b) H. Reimlinger, *Chem. Ber.*, **100**, 3097 (1967); (c) H. Dürr, L. Schrader, and H. Seidl, *ibid.*, **104**, 391 (1971).



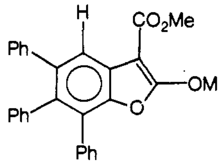
	% yield (35)
a, R = R¹ = R² = R³ = Ph	85
b, R = R³ = Ph; R¹ = R² = H	86
c, R, R¹ = C_6H_4; R² = R³ = Ph	30
d, R = H; R¹ = R² = R³ = Ph	0

supported by the observation that the spiro compounds **34** give the methyl 1*H*-indazole-3-carboxylates **37** as illustrated in the scheme. The second step of the sequence, 1,2 migration of a carbomethoxy group, is perhaps more contentious although not unprecedented; the first such migration was recently reported.[22] The German workers reasonably suggest that the reaction is initiated by n → π* excitation of the nitrogen-nitrogen double bond at 360 nm, and they have shown that the reaction proceeds from the triplet excited state. Furthermore, they argue in favor of direct formation of the diradical from the indazole. This direct route (**34** → **36** → **25** → **35**) would require two photons per molecule while the alternative, *via* the diazo compound, would require an additional photon per molecule and a loss of aromaticity. Although this argument has merit, there is insufficient evidence presently available to determine whether **25** is formed directly or indirectly from the 3*H*-indazole.

SCHEME III



The photolysis of **34c** proceeds in low yield (30%) to the only naphthocyclopropene yet reported. On the other hand, **34d** is anomalous in that it gives the benzofuran derivative **38**. Compounds with this general structure result from thermal rearrangement of benzocyclopropene-7-carboxylates;[12,20] the factors governing this latter variation of the spiro-3*H*-pyrazole photolysis are not yet known.



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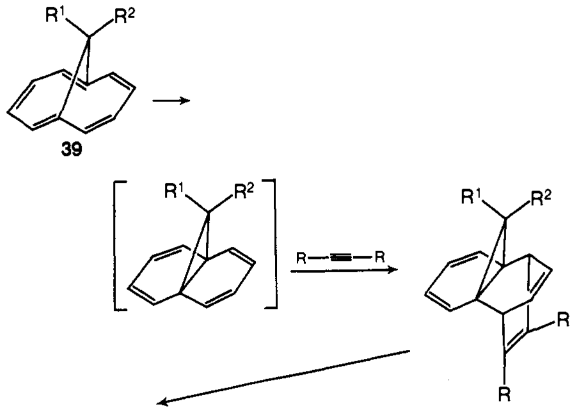
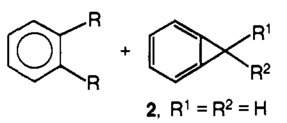
C. Retrodiene Reactions

The first nonphotochemical synthesis of benzocyclopropenes resulted from the work of Vogel, *et al.*, with 1,6-methano[10]annulene derivatives **39**.[23] These bridged cyclodecapentaenes generally undergo Diels–Alder addition with a variety of dienophiles *via* the norcaradiene valence-bond tautomer.[23,24] The resultant product has the ring system **40** which retains a norcaradiene moiety. On pyrolysis the 1:1 adducts of 1,6-methano[10]annulene with dimethyl acetylenedicarboxylate and dicyanoacetylene (**40a,b**) undergo retrodiene cleavage to give benzocyclopropene (**2**) in yields of 45 and 68%, respectively.[25,26] Similarly, the adduct of 11,11-difluoro-1,6-methano-[10]annulene and dicyanoacetylene (**40d**) undergoes almost complete Alder–Rickert cleavage at 380° and 10^{-4} Torr to give 7,7-difluorobenzocyclopropene (**42**) in high yield.[24] Adduct **40c** appears to give 7-fluorobenzocyclopropene (**41**), but this compound is highly reactive and readily gives benzaldehyde with moisture.[27] The method has only been successful for benzocyclopropenes that exhibit moderate thermal stability and attempts to synthesize several geminal disubstituted and 7-monosubstituted derivatives (*e.g.*, 7,7-dimethyl, 7-bromo, 7-chloro, 7-cyano, and 7-carbomethoxy) have failed completely.[24-27]





2, R¹ = R² = H
41, R¹ = F; R² = H
42, R¹ = R² = F

40a, R = CO_2Me; R¹ = R² = H
b, R = CN; R¹ = R² = H
c, R = CN; R¹ = F; R² = H
d, R = CN; R¹ = R² = F

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[22] M. J. Jorgenson and T. J. Clark, *J. Amer. Chem. Soc.*, **90**, 2188 (1968).

[23] E. Vogel, *Chem. Soc., Spec. Publ.*, **No. 21**, 113 (1967).

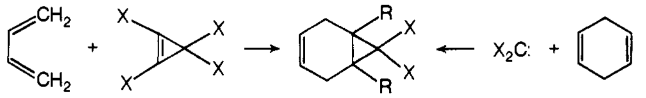
[24] E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem.*, **80**, 279 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 289 (1968).

[25] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

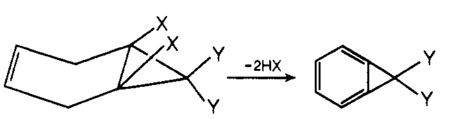
[26] S. Korte, Ph.D. Thesis, University of Köln, 1968.

D. Bicyclo[4.1.0]heptenes as Precursors

Bicycloheptenes have recently been used as precursors to benzocyclopropenes, and the syntheses so far devised are attractive in that the steps involved are few and the product yields satisfactory. The starting materials for synthesis, bicyclo[4.1.0]hept-3-enes (**43**), are generally easy to obtain, as is illustrated by the Diels–Alder addition of tetrahalogenocyclopropenes to dienes[28] and carbene addition to cyclohexa-1,4-dienes.[29] Dehydrohalogenation of the 1,6,7,7-tetrahalogeno derivatives obtainable by the former route would appear to offer a simple synthesis of 7,7-dihalogenobenzocyclopropenes. This is exemplified by the formation of *gem*-difluorobenzocyclopropene (**42**) in 40% yield by dehydrobromination of **44a** with potassium hydroxide in triethylene glycol.[24] Dehydrochlorination of **44b** affords **42** in only 20% yield.[27]



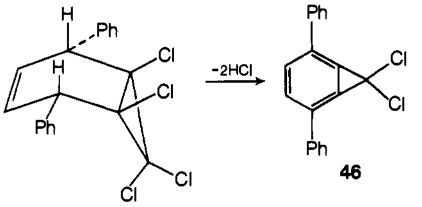
43, R = H or X



44a, X = Br; Y = F
b, X = Cl; Y = F
c, X = Y = Cl

42, Y = F

Attempted dehydrochlorination of **44c**, under a variety of conditions, gave rise to a complex mixture of products which did not contain the desired 7,7-dichlorobenzocyclopropene.[27,30] On the other hand, treatment of the 1,5-diphenylbicycloheptene **45** with potassium *tert*-butoxide in tetrahydrofuran results in smooth dehydrochlorination and formation of 7,7-dichloro-2,5-diphenylbenzocyclopropene (**46**) in almost quantitative yield.[31] In this case the reaction is undoubtedly assisted by the phenyl substituents which can stabilize any development of carbanion character at the benzylic position.



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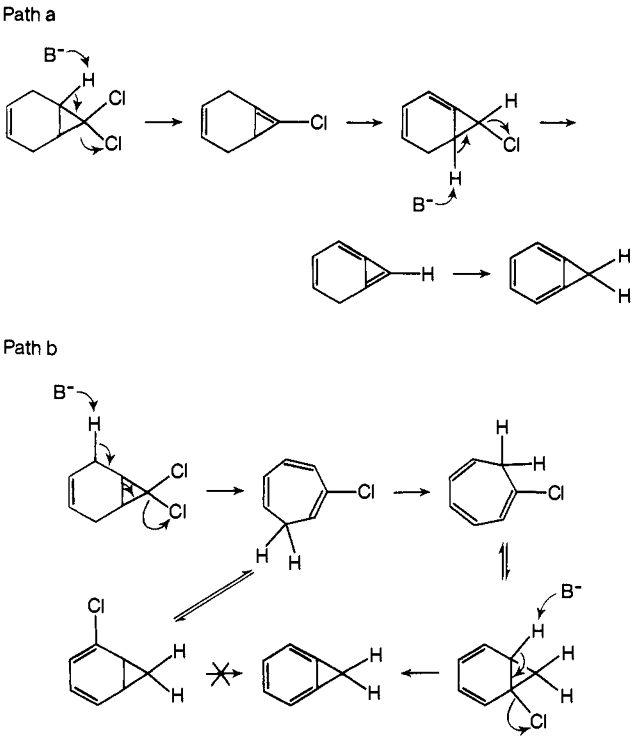
46

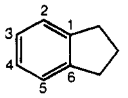
Benzocyclopropene has recently been prepared[32] in 40% yield by dehydrochlorination of 7,7-dichlorobicyclo-[4.1.0]hept-3-ene. The elimination reaction is clearly more complex than the simple cases discussed above, and highly strained species have been suggested as reaction intermediates (path a, Scheme IV). Nevertheless, it is more probable that a greater driving force for reaction would result from the relief of strain gained by formation of 3-chlorocycloheptatriene (path b, Scheme IV). This compound could undergo a series of [1,5] hydrogen shifts and the failure of the reaction to yield a chlorocycloheptatriene can be taken to reflect the known[33] equilibrium between a cycloheptatriene and a norcaradiene. Thus 2-chlorocycloheptatriene, formed by a single [1,5] hydrogen shift in the 3 isomer, will be in equilibrium with 1-chloronorcaradiene, and, under the reaction conditions, this latter compound can undergo dehydrochlorination to give the observed product.

SCHEME IV

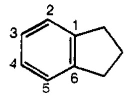


III. Physical and Theoretical Aspects of Benzocyclopropenes

Perhaps the greatest stimulus to the study of benzocyclopropene chemistry is the expectation that partial bond fixation should result from the accommodation of the aromatic sextet in the strained ring system. The earliest prediction of aromatic bond localization was made in 1930 by Mills and Nixon[34] to explain certain differences in the chemical reactivities in indan and tetralin. Their postulate was that the strain associated with the fusion of a five-membered ring to a benzene nucleus would cause partial fixation of the aromatic bonds in the direction indicated by the structure **47a**. The experimental data on which the Mills–Nixon effect was based were subsequently shown to be ambiguous,[35] and a theoretical study of the bond length and bond angle strains in indan, by Coulson and Longuet-Higgins,[36] led to the conclusion that the alterna-



47a



47b

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(27) E. Vogel, private communication.

(28) D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90**, 2376 (1968).

(29) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).

(30) P. K. Coveny and B. Halton, unpublished observations.

(31) B. Halton and P. J. Milsom, *Chem. Commun.*, 814 (1971).

(32) W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Commun.*, 1461 (1971).

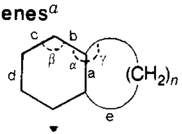
(33) See, for example, H. Günther, B. D. Tunggal, M. Regitz, H. Scherer, and T. Keller, *Angew. Chem.*, **83**, 585 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 563 (1971). For a review, see G. Maier, *Angew. Chem.*, **79**, 446 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

(34) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(35) See G. M. Badger, *Quart. Rev., Chem. Soc.*, **5**, 147 (1951).

(36) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **42**, 756 (1946).

TABLE I. CNDO/2 Calculated Geometries of Some Benzocycloalkenes[a]

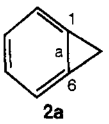


n	*a*	*b*	*c*	*d*	*e*	α	β	γ
1	1.420	1.365	1.400	1.382	1.458	122.6	114.8	60.8
2	1.421	1.379	1.391	1.381	1.476	121.4	116.5	91.5
3	1.412	1.389	1.386	1.384	1.472	119.8	119.8	109.7
4	1.403	1.392	1.383	1.383	1.470	118.7	122.0	121.4

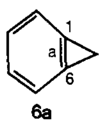
[a] Data taken from ref 5. Bond lengths are in angstrom units and angles are in degrees.

tive structure **47b** should be more favored. These molecular orbital calculations predict a shortening of the 1–6 bond and a lengthening of the 3–4 bond together with a widening of the C_2–C_1–C_6 and a compression of the C_1–C_2–C_3 bond angles, respectively. Similar bond-length and bond-angle variations can therefore be expected for the more highly strained benzocycloalkenes. The direction of aromatic bond fixation has generally been assumed in line with the above-mentioned theory although there are no sufficiently accurate X-ray crystallographic data available to substantiate this at the present time. No structure determination has been performed on a benzocyclopropene, but data for dichlorobenzocyclobutene[37] and benzo[1,2:4,5]dicyclobutene[38] have been recorded. The bond-length data obtained in both these studies showed differences from the normal benzene bond length (1.395 Å), but the levels of refinement were such (bond lengths ± 0.02 Å) that both groups of investigators felt the differences to be insufficient to claim any bond localization. However, in both cases bond angle changes were observed in accord with the Longuet-Higgins–Coulson predictions.[36]

More recent theoretical work now places considerable doubt on the direction of aromatic bond fixation predicted for indan and assumed for the more strained benzocycloalkenes. Manatt and coworkers have calculated the geometries of the benzocycloalkenes using the CNDO/2 (complete neglect of differential overlap) semiempirical molecular orbital method,[5] and the results of the treatment are shown in Table I. The striking feature of these results is the prediction of an increase in the length of the 1–6 bond (bond a, Table I) in the strained benzocycloalkenes, with bond localization throughout the series in the direction originally proposed by Mills and Nixon, *i.e.*, as in **2a** and not **6a.** The direction of bond angle change is, however, consistent with the earlier theory, although a comparison of the calculated angles with the available experimental data suggests that the calculations somewhat underestimate the magnitude of these changes. The authors suggest that bond a in benzocyclopropene could be overestimated by ca. 0.025 Å, but they stress that the direction of bond fixation is far more important than the magnitude of the changes involved. Significance can be attached to these results since the same program leads to calculated geometries, for a series of cycloalkenes and polycyclic aromatics, with bond lengths accurate to ±0.008 Å when compared with the experimental data.[39]



2a



6a

Further support for the results of Manatt and coworkers stems from a series of independent calculations performed to examine the bonding patterns in benzocyclopropene and the benzocyclopropenyl cation, anion, and radical.[40] For the SCC-EH (self-consistent charge extended Hückel) molecular orbital approach used, three distinct geometries were assumed and three series of calculations were performed. In series i the geometry calculated by Manatt[5] was imposed, while in series ii an approximation of the alternative structure **(6)** with shortened 1-6, 2-3, and 4-5 bonds was used. For series iii the 1-6 bond was further reduced to the length of a cyclopropene double bond. The last case gave rise to a neutral molecule with π-electron localization which was significantly less stable than those with alternative geometries. The calculations in series i and ii gave rise to neutral molecules with comparable stabilities, but significant aromatic bond fixation was only predicted for series i where the 1–6 bond was lengthened. Surprisingly, with a shortened 1–6 bond (series ii) almost no bond localization was predicted. However, series i led to the most stable cation which also had the greatest degree of charge distribution. On the basis of these results, and the necessity for bond fixation to account for the nmr spectrum (see below), it has been concluded that aromatic bond fixation results in a lengthening of the 1–6 bond.[5,40] Throughout this review we have elected to use a representation for the benzocyclopropenes consistent with the CNDO/2[5] and SCC-EH[40] results rather than with the earlier predictions.[36] However, it should be stressed that the direction of aromatic bond localization will remain uncertain until such time as accurate structure determinations are performed.

Several theoretical treatments on the relative stabilities of strained hydrocarbon systems have included benzocyclopropene.[41] However, a regular hexagon has inevitably been used for the six-membered ring of benzocyclopropene, and the results do not justify discussion here.

The concept of aromatic bond fixation is necessary in order to give an empirical explanation of the nmr proton–proton, spin–spin coupling constants of the aromatic protons of benzocyclopropene and its derivatives. The 60-MHz spectrum of benzocyclopropene is simple in that it exhibits slightly broadened singlets at δ 7.12 and 3.11 in a ratio of 2:1 for the aromatic and methylene protons, respectively.[25] The resonance of the six-membered ring protons in the normal aromatic region indicates that the diamagnetic ring current in benzocyclopropene is not disturbed to any significant extent when compared with that of normal aromatic molecules. The ^{13}C–H coupling constant for the methylene protons, determined as 178 ± 2 Hz, is comparable with the value measured for 1-methylcyclopropene (172 Hz)[6] and can be taken to reflect similar bond angles at C_3 and C_7 in cyclopropene and benzocyclopropene, respectively.[6,42]

A planar, or near-planar, ring structure for the benzocyclopropenes is inferred from the magnetic equivalence of identical substituents at the 7 position. Thus methyl 7,7-dimethylbenzocyclopropene-3-carboxylate **(21)** exhibits a six-proton singlet for the *gem*-dimethyl group which

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(37) G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72,** 668 (1968).

(38) J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B*, **25,** 978 (1969).

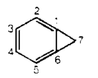
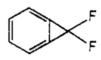
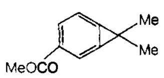
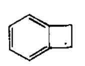
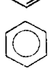
(39) C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27,** 689 (1971).

(40) B. Halton and M. P. Halton, unpublished results.

(41) H. S. Lee, *Hua Hsueh*, 69 (1963); N. Tyutyulov and F. Fratev, *Monatsh. Chem.*, **97,** 969 (1966).

(42) K. Mislow, *Tetrahedron Lett.*, 1415 (1964).

TABLE II. Nmr Coupling Constants of Benzocyclopropenes and Related Compounds[a]

Compound	J_{23}	J_{24}	J_{25}	J_{34}
 (2)	6.04[b]	0.33	1.85	7.63
 (42)	6.83[b]	0.32	1.89	7.43
 (21)	6.6[c]	0.7	1.9	
	7.36[b]	1.00	1.03	7.79
	7.56[d] (ortho)	1.38 (meta)	0.68 (para)	

[a] Coupling constants in hertz. [b] Data taken from ref 43. [c] Data taken from ref 4. [d] H. Günther, *Tetrahedron Lett.*, 2967 (1967).

is maintained even at −150°.[4] Similarly, the ^{19}F nmr spectrum of the 7,7-difluoro derivative **42** shows two equivalent fluorine atoms coupled to the ortho aromatic protons at C_2 and C_5 ($J = 3.4$ Hz).[24]

At 100 and 220 MHz,[43] the nmr spectrum of **2** shows the aromatic resonance to be of the AA′BB′ type[44] with the ortho protons coupled to the methylene group ($J \sim 1$ Hz). An AA′BB′ system centered at δ 7.54 is also exhibited by **42.**[45] The analysis of these spectra, by computing and matching procedures,[43] shows that the proton-proton, spin-spin coupling constants are affected by the strain associated with the ring system (Table II). The most interesting feature of these data is the observation that J_{24} (J_{meta}) is less than J_{25} (J_{para}) for the benzocyclopropenes, while normal aromatics have precisely the reverse order (*cf.* benzene). In benzocyclobutene these values are comparable. Thus the trends in the coupling constants of the benzocycloalkenes show that J_{23} (J_{ortho}) is generally insensitive to strain except for the benzocyclopropenes where the value is reduced by as much as 1.5 Hz. As the strain is increased there is a marked increase in J_{para} while J_{meta} decreases sharply. These latter trends were intially rationalized[43] by a consideration of aromatic bond fixation in the direction illustrated by **6.** However, these same authors have subsequently pointed out[5] that bond fixation in either sense, **2** or **6,** accounts for the changes equally well, the decisive factor being a shift away from a fully delocalized π-electron system. The general insensitivity of J_{ortho} to strain was thought to be due[43] to opposing bond angle and bond length factors which would cancel in structure **6** but not in **2.** On the other hand, extended Hückel MO theory suggested that the small changes in J_{ortho} could be due to bond angle factors alone.[43] In fact, Manatt, *et al.*, have calculated the coupling constants in the benzocycloalkenes by using their calculated geometries (Table I) and adopting the CNDO/2 approach.[5] While absolute values are not obtained by the method, the observed trends and relative magnitudes of J_{ortho}, J_{meta}, and J_{para} are reproduced by the molecular orbital method. In particular, the lowered value of J_{ortho} observed for benzocyclopropene is faithfully reproduced by the calculation, despite bond localization in the opposite sense to that used in the earlier arguments.

TABLE III. Ultraviolet Spectra of Some Benzocyclopropenes

Compound	Solvent	λ_{max}, nm	Log ϵ	Ref
Benzocyclopropene	C_6H_{12}	252	2.7	26
		258	3.0	
		264	3.2	
		270	3.4	
		277	3.3	
7,7-Difluorobenzocyclopropene	C_6H_{12}	242	2.5	24
		246	2.8	
		252	3.0	
		258	3.1	
		264	2.9	
Methyl 7-methylbenzocyclopropene-7-carboxylate	C_2H_5OH	262	2.6	49
		267	2.7	
		274	2.7	
Methyl 7,7-dimethylbenzocyclopropene-3-carboxylate	CH_3OH	238	3.9	4
		279	3.4	
		286	3.4	
7,7-Diethyl-2,5-diphenylbenzocyclopropene	C_6H_{12}	291	4.3	53
		298	4.3	
		320	4.0	
7,7-Dichloro-2,5-diphenylbenzocyclopropene	C_6H_{12}	316	4.7	31

TABLE IV. Aromatic Double Bond Stretching Vibrations of Some Benzocyclopropenes and Cyclopropenes

Compound	Frequency, cm^{-1}	Ref
Benzocyclopropene	1666	25
7,7-Difluorobenzocyclopropene	1655	27
7,7-Dichloro-2,5-diphenylbenzocyclopropene	1685	31
7,7-Diethyl-2,5-diphenylbenzocyclopropene	1660	53
Cyclopropene	1641	49
3,3-Dimethylcyclopropene	1632	49
3,3-Dimethyl-1-phenylcyclopropene	1740	49
Tetraphenylcyclopropene	1820	18

Nmr spectra of oriented benzocyclopropene and the *gem*-difluoro derivative have been determined.[46] The results of this study show that, within experimental error, the six-membered rings of both compounds have identical proton geometry. Furthermore, bond angle distortions are predicted to be in the same directions as have been calculated.[5,36]

The ultraviolet spectra of the benzocyclopropenes (Table III) do not differ appreciably from those of either their benzene or benzocyclobutene counterparts. Thus the electronic spectra of benzocyclopropene and benzocyclobutene are similar, not only to each other,[25] but also to that of o-xylene. These results infer that the bond angle and bond length changes associated with the strained ring systems cannot be disrupting the aromatic chromophore to any great extent.

The infrared spectra of benzocyclopropenes are notable for their simplicity, indicating the high degree of symmetry in the molecules. The most significant single feature of the spectra is the presence of an intense band at ca. 1670 cm^{-1} (see Table IV). This band has invariably been described as an "aromatic double bond" stretching vibration even though its position is considerably shifted from the normal range for substituted benzenes (1590–

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(43) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).

(44) See, for example, L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, p 134.

(45) The nmr data reported by Vogel, *et al.*, in ref 24 have now been further refined; see ref 43.

(46) J. B. Pawliczek and H. Günther, *J. Amer. Chem. Soc.*, **93**, 2050 (1971), and references cited therein.

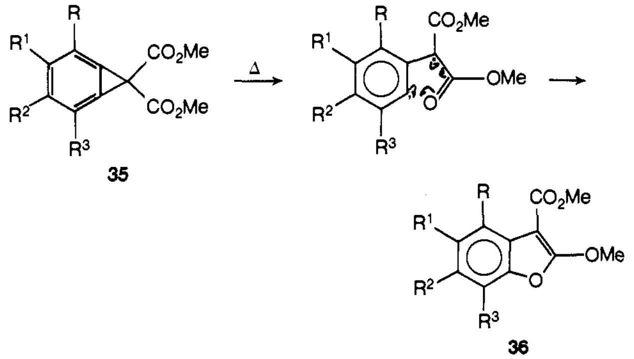
1610 cm^{-1}). A similar effect is observed with cyclopropene,[47] where a medium intensity band is observed at 1641 cm^{-1} compared with 1566 and 1611 cm^{-1} for cyclobutene and cyclopentene, respectively.[48] Closs has emphasized[49] that this cyclopropene band is a skeletal ring vibration containing a substantial component of double bond stretching, and it is reasonable to expect similar coupling of a three-membered ring vibration with an aromatic bond vibration in benzocyclopropene.

The position of the double-bond vibration in cyclopropene is highly dependent on the nature of the vinyl substituents, but only slightly dependent on the substituents at the 3 position (Table IV). The former effect cannot be present in the benzocyclopropenes, and no detailed study has been made of the influence of the 7 substituents on the "aromatic double bond" stretching frequency.

IV. Reactions of Benzocyclopropenes

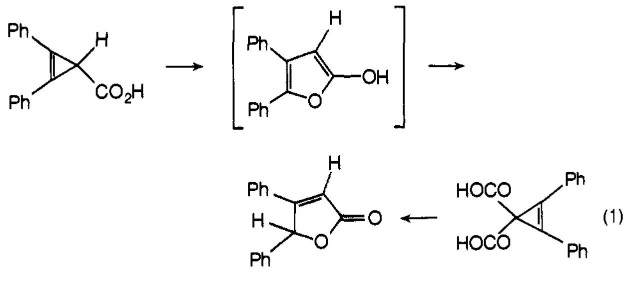
The chemistry of the benzocyclopropenes is dominated by reactions involving cleavage of the three-membered ring. The estimated[3] strain energy of the ring system shows benzocyclopropene to be less stable than cyclopropene[50] by more than 18.3 kcal mol^{-1}, and this is reflected by the ease with which ring-opening reactions proceed. Relatively few examples of reactions are known where the integrity of the ring system is maintained and the effects of ring strain on aromatic substitution patterns, observed for the benzocyclobutenes,[51] have not been determined. Cycloaddition reactions with benzocyclopropene have been effected[26] and provide chemical evidence for partial aromatic bond fixation.

The thermal ring opening reactions of the benzocyclopropenes are believed to proceed by homolysis of the single bond,[12] with the resultant 1,3-diradical undergoing stabilization by one of a variety of routes dependent on the nature of the 7 substituents. The 7-carboxylate derivatives **35** readily rearrange to the benzofurans **38** when heated at temperatures above their melting points.[20] The rearrangement has its parallel in cyclopropene chemistry where the 1,2-diphenyl-3-carboxylic acid derivative gives rise to diphenylcrotonolactone[52] (eq 1). Similarly, the benzocyclopropene-7,7-dicarboxylic acid **48** gives the lactone **49** by a process analogous to the rearrangement and decarboxylation of the corresponding cyclopropene diacid.

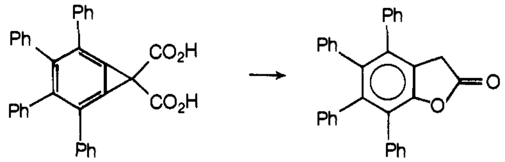


35

36

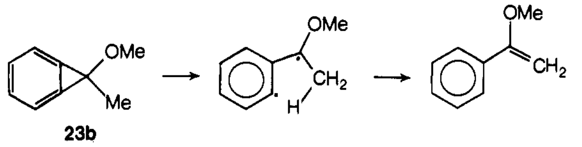


(1)

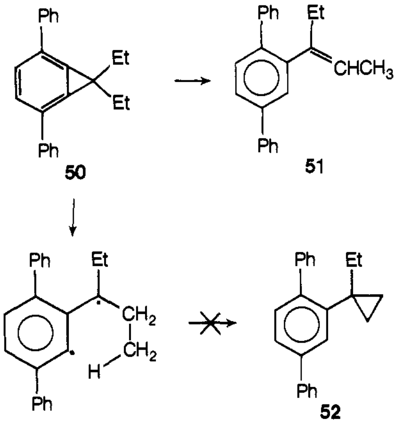


48 **49**

When one of the 7 substituents of the benzocyclopropene contains an α-hydrogen atom, hydrogen transfer through a five-membered transition state takes place. The product of reaction is a substituted styrene as demonstrated by the quantitative rearrangement of 7-methoxy-7-methylbenzocyclopropene **(23b)** at room temperature (eq 2).[12] Mild thermolysis of the 7,7-diethyl derivative **50** leads to more than one reaction product, but the major component of the mixture, identified as the olefin **51**, again corresponds to α-hydrogen transfer.[53] No evidence for products such as **52**, formed by β-hydrogen transfer through a six-membered transition state, could be found.

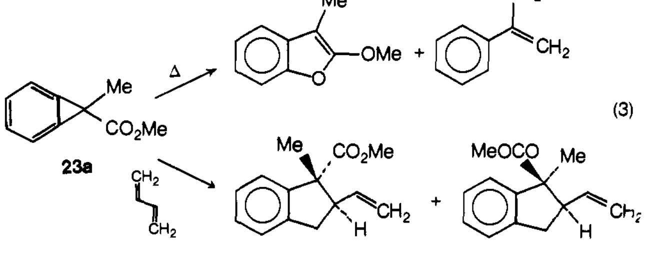


23b (2)



50 **51** **52**

It is not surprising that **23a**, with alkyl and carbomethoxy substituents, gives benzofuran and styrene products. The rearrangement has been successfully intercepted by the addition of butadiene to give the two possible isomeric indans[12] (eq 3). This observation lends strong



23a (3)

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(47) K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961).

(48) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958.

(49) See ref 6, pp 70–75.

(50) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 3980 (1962).

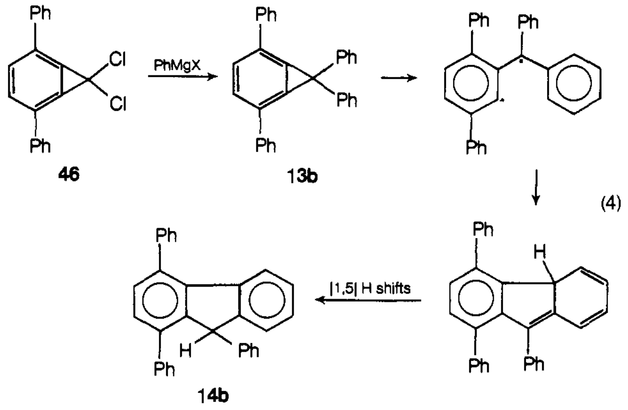
(51) R. D. Rieke, *J. Org. Chem.*, **36**, 227 (1971), and references cited therein.

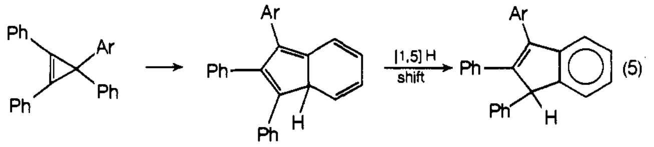
(52) R. Breslow, R. Winter, and M. A. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(53) B. Halton and A. D. Woolhouse, unpublished observations.

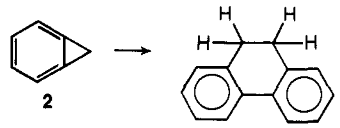
support to the intervention of a 1,3-diradical and argues against a concerted process. Furthermore, the rearrangement of **23a** follows first-order kinetics with a rate constant independent of added butadiene, suggesting that unimolecular ring opening is the rate-determining step. The activation energy, measured as 25 kcal mol^{-1}, represents the lower limit for the energy of the benzocyclopropene single bond.[6]

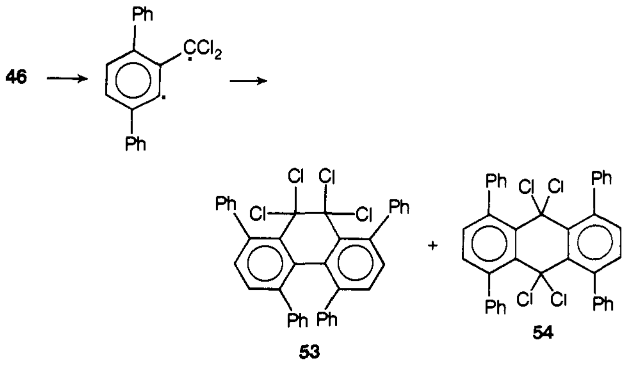
The only known 7-arylbenzocyclopropene, 2,5,7,7-tetraphenylbenzocyclopropene **(13b)**, is particularly labile and has only been identified by its spectroscopic data and its mode of formation from the corresponding 7,7-dichloro derivative **(46)**.[11] All attempts to isolate the pure compound resulted in the formation of 1,4,9-triphenylfluorene **(14b)**. In this case the rearrangement can be rationalized by cyclization at a vacant ortho site of an aromatic ring attached to C_7, with the formation of an isofluorene (eq 4). Two thermally allowed [1,5] hydrogen shifts would then give rise to the observed product. The rearrangement is analogous to those reported for the tetraarylcyclopropenes (eq 5),[17,18] but proceeds efficiently at temperatures some 140° lower.

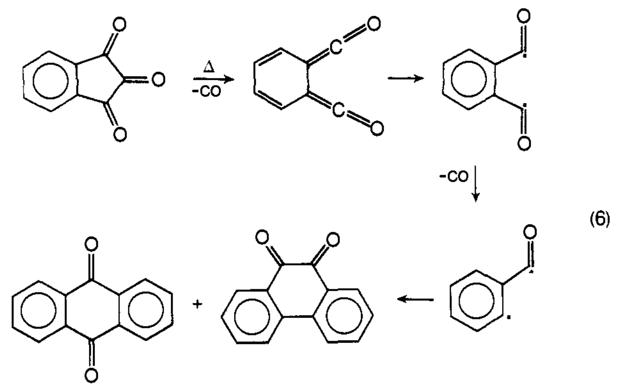




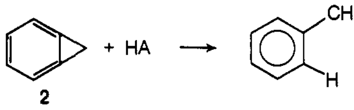
Benzocyclopropene has greater thermal stability than the simple 7,7-disubstituted derivatives discussed above, decomposing when distilled at atmospheric pressure.[25]' At 80°, vapor-phase pyrolysis of **2** leads to 9,10-dihydrophenanthrene in 40% yield and the diradical intermediate has been trapped with butadiene.[26] The 7,7-dichloro derivative **46** behaves in an analogous fashion, but in this case, heating the compound in the melt results in two dimeric products whose structures are proposed as the "head-to-head" and "head-to-tail" dimers **53** and **54**, respectively.[11] The appearance of two products is supported by the isolation of 9,10-anthraquinone and 9,10-phenanthraquinone in the pyrolysis of indantrione (eq 6),[54] and it is somewhat surprising that 9,10-dihydroanthracene is not obtained in the pyrolysis of **2**.







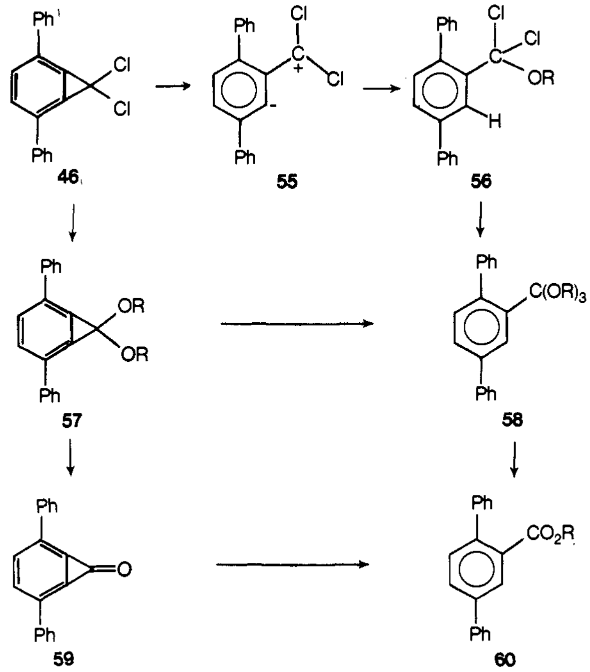
The benzocyclopropenes, like the cyclopropenes,[6] are sensitive to acid reagents and give rise to ring open products as demonstrated by **2**.[26] The *gem*-dichloro compound **46** is rapidly converted to methyl 2,5-diphenylbenzoate **(60)** when treated with methanol.[31] The formation of this product has been represented by the path **46** → **56** → **58** → **60** (Scheme V) involving solvent addition to the single bond of the benzocyclopropene, either directly or to the ring-opened species **55**, and subsequent ready solvolysis of the benzylic chlorine atoms of **56**. Support for this route comes from the isolation of the ortho ester **58**, in quantitative yield, when the reaction is performed in



2

A = $CH_3CO_2^-$, $PhCO_2^-$, or Cl^-

SCHEME V



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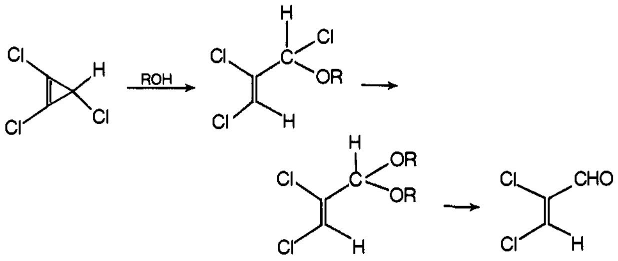
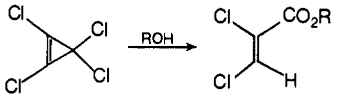
(54) R. F. C. Brown and R. K. Solly, *Aust. J. Chem.*, **19**, 1405 (1966).

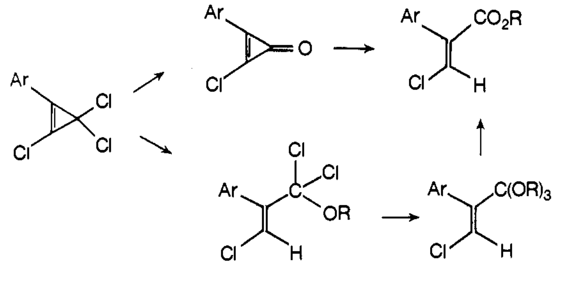
the presence of excess added base such as triethylamine. In the absence of base, the protons generated in the solvolysis step are available to catalyze the decomposition of the ortho ester **58** to the carboxylic ester **60** with moisture. The ease with which the benzocyclopropene single bond is cleaved argues against formation of **58** *via* **57**. An alternative path to the carboxylic ester **60** is by way of the benzocyclopropenone **59** (Scheme V). Although benzocyclopropenones have not been isolated, species with the same symmetry have been generated in solution and give methyl benzoates with methanol.[55,56] However, the presence of triethylamine would not be expected to divert this reaction to ortho ester, and it must be concluded that benzocyclopropenones are unlikely intermediates in the solvolytic ring cleavage of the *gem*-dihalogenobenzocyclopropenes.[11,31] Like the *gem*-dichloro compound, 7-fluorobenzocyclopropene **(41)** is also highly reactive and, in the presence of moisture, affords benzaldehyde;[27] the formation of this product is readily explained by the route outlined above for **46**.

The formation of aldehyde from **41** and ester and ortho ester from **46** parallels the behavior of 1,2,3-trichlorocyclopropene in methanol.[57] The initial product of reaction is the unstable acetal **61** which gives the corresponding aldehyde on standing. The ring opening of tetrachlorocyclopropene[58,59] and 1-aryltrichlorocyclopropenes[60,61] in alcohols are also similar. In the latter case (eq 7), the mechanism of the reaction is not known with certainty, but it has been suggested[60] that cyclopropenones may be reaction intermediates. However, experiments to terminate the reaction at the ortho ester stage do not appear to have been performed. Support for the path involving direct solvolysis to the ketone comes from the well-established route to cyclopropenones from 1,2-diaryl-3,3-dichlorocyclopropenes.[60-62]



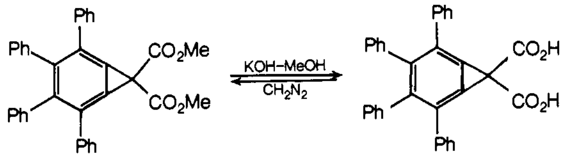
61



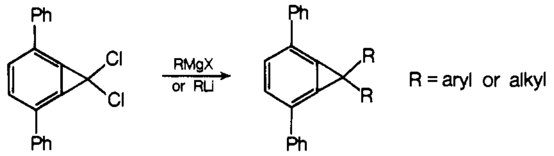


(7)

Only two reactions have been reported in which the benzocyclopropene ring system is maintained. The 7,7-diester **35a** is hydrolyzed to the diacid **48** without rearrangement, and the reaction is reversed with diazomethane.[20] The *gem*-diphenyl and -diethyl derivatives, **13b** and **50**, result from reaction of Grignard or organolithium reagents with **46**.[11,53] Other geminal disubstituted derivatives can be generated by these reactions, but, more often than not, their stability has precluded isolation, and rearrangement products are obtained.[53]



35a **48**

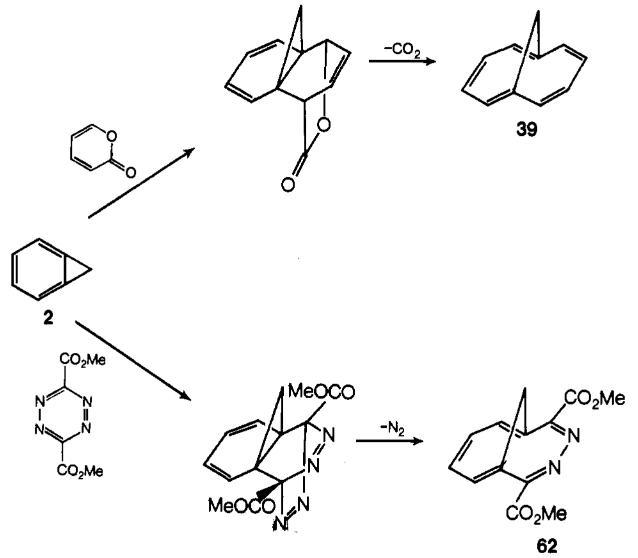


46

13b, R = Ph
50, R = Et

Benzocyclopropene undergoes cycloaddition reactions with a variety of dienes.[26] Thus **2** reacts with α-pyrone and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate to give, as the final product of reaction, 1,6-methano[10]annulene **(39)** and the diaza diester analog **62**, respectively (Scheme VI). Cycloaddition of benzocyclopropene with butadiene has been effected,[26] but, under the conditions employed, the ring-opened diradical was also trapped as shown in Scheme VII. The formation of cycloaddition products provides chemical evidence for partial aromatic bond fixation in the benzocyclopropenes. However, the results do not allow conclusions to be drawn as to the direction of bond localization, because cycloaddition across the 1–6 bond can be rationalized[16] either as a

SCHEME VI



39

2

62

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(55) J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc. C*, 981 (1971); *Chem. Commun.*, 221 (1969).

(56) M. S. Ao, E. M. Burgess, A. Schauer, and E. A. Taylor, *Chem. Commun.*, 220 (1969).

(57) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **88**, 2478, 2481 (1966).

(58) S. W. Tobey and R. West, *Tetrahedron Lett.*, 1179 (1963).

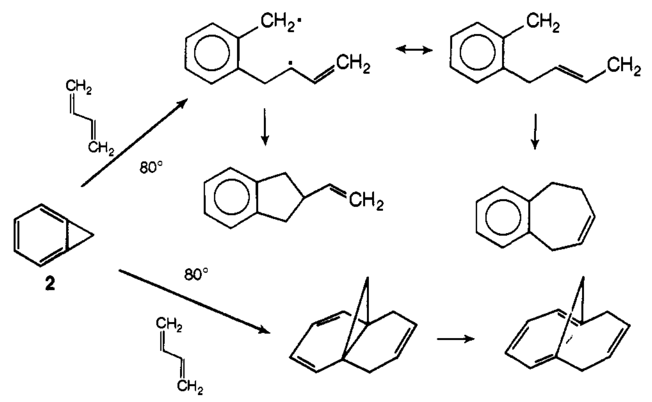
(59) The reaction of tetrachlorocyclopropene with protic solvents is discussed in ref 58 in terms of solvent addition to the double bond, followed by ring opening of the unstable cyclopropane. However, the subsequent isolation of the acetal **61** from 1,2,3-trichlorocyclopropene is consistent with ring cleavage as the initial step (see ref 57), and the same mechanism may well operate in both cases.

(60) R. West, D. C. Zecher, and S. W. Tobey, *J. Amer. Chem. Soc.*, **92**, 168 (1970).

(61) R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

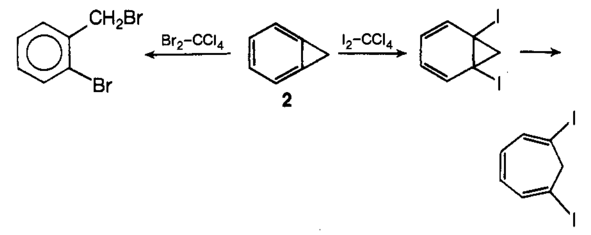
(62) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 4215 (1964).

SCHEME VII

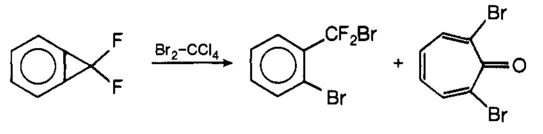


symmetry allowed [$_{\pi}6_s$ + $_{\pi}4_s$] process for **2** or a [$_{\pi}2_s$ + $_{\pi}4_s$] process for **6**.

Addition reactions of the halogens with benzocyclopropene have been observed.[25-27] Isolation of 2,7-diiodocycloheptatriene, from the reaction of **2** with iodine, can be rationalized in terms of the bond localized structure and presumably arises *via* the norcaradiene (eq 8). With bromine, the reaction takes a different course giving the simple ring-opened product. In contrast, the 7,7-difluoro derivative gives rise to both types of products with bromine although, surprisingly, the fluoro substituents are hydrolyzed during work-up and 2,7-dibromotropone is isolated (eq 9).[27]



(8)

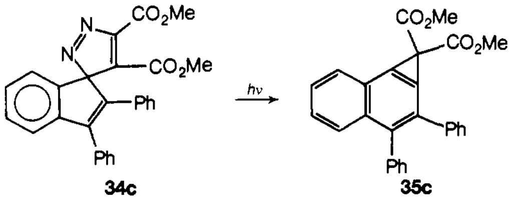


(9)

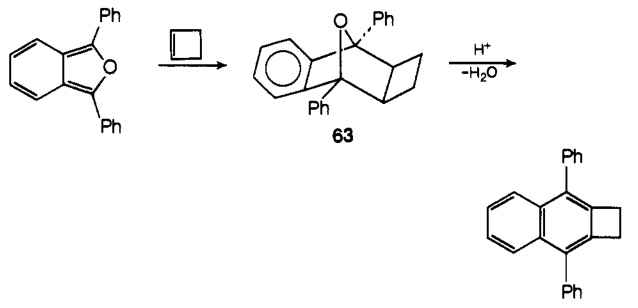
V. Derivatives

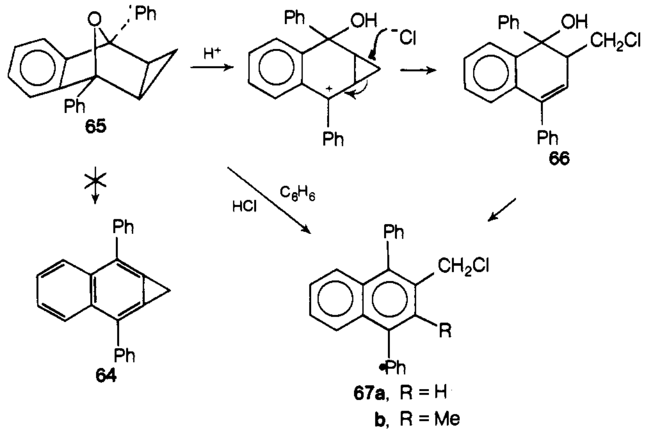
A. Naphthocyclopropenes

The only naphthocyclopropene known is the naphtho[a]cyclopropene **35c**, prepared by the spiro-3*H*-pyrazole route.[20] The chemical and spectroscopic properties of this compound do not appear to differ significantly from the benzocyclopropene analogs, but no structural data are available and the direction of aromatic bond fixation, presumed to be in the direction shown, has been neither determined nor predicted.



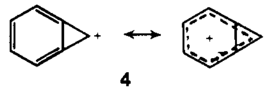
Attempts to synthesize the naphtho[*b*]cyclopropene ring system **64**, by a route parallel to the successful[63] synthesis of naphtho[*b*]cyclobutene from **63**, have failed.[64] Dehydration of the exo-cyclopropene adduct **65**, with hydrogen chloride in benzene, afforded the chloromethylnaphthalene **67a** as the sole product of reaction. The formation of this product can be explained by the intervention of the naphtho[*b*]cyclopropene **64** which adds hydrogen chloride across the single bond. However, under milder conditions, **65** gave the alcohol **66** which was readily dehydrated to **67a**. The adduct between 1-methylcyclopropene and 1,3-diphenylisobenzofuran would not be expected to yield a naphthocyclopropene, but this compound was found to behave in a manner strictly analogous to **65**, giving the methyl-substituted naphthalene **67b**. As a result of these and further dehydration experiments, the authors conclude that naphtho[*b*]cyclopropene **64** is not an intermediate in these processes.[64]





B. Benzocyclopropenyl Cation

The cation **4** derived from benzocyclopropene has yet to be characterized even though it received theoretical consideration as early as 1952. Simple Hückel molecular orbital calculations[65] predict stabilization of the benzocyclopropenyl cation, radical and anion by 3.65, 3.24, and 2.83 β, respectively. However, this simple treatment is unlikely to provide reliable estimates of the stabilities of these species because of the highly strained nature of the ring system and the inherent neglect of the σ framework by this method. Nevertheless, stabilization is to be expected and, for the cation, charge delocalization through the bridged ring system should result in an aromatic ion.



4

More recent SCC-EH calculations,[40] employing the calculated[5] geometry of benzocyclopropene (**2a**) (Table

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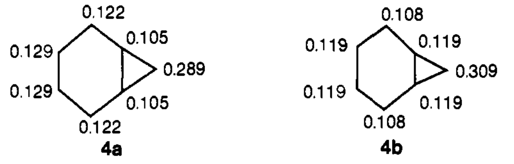
[63] C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Justus Liebigs Ann. Chem.*, **653**, 79 (1962).

[64] M. P. Cava and K. Narasimhan, *J. Org. Chem.*, **36**, 1419 (1971).

[65] J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952).

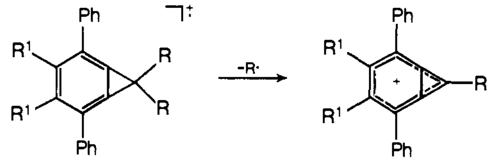
I) and an estimate of the bond switch isomer **6a** (see section III), lead to the charge distribution shown in **4a** and **4b**, respectively, for the benzocyclopropenyl cation. The residual charge of the C_7-H unit is found to be similar in both cases, but delocalization away from the three-membered ring is greater for **4a** (50.2 *vs.* 45.4%) and is more evenly distributed over the C-H units from C_2 to C_5. However, the overriding result of the calculations is the lower *total* energy of **4a** compared with **4b**, and this has been taken as support for the recently calculated[5] geometry of the neutral molecule. It is interesting to note that in both cases examined, the π-electron overlap populations predict bond localization between C_2-C_3 and C_4-C_5, indicative of partial 1,3-diene character in the cation. The calculations indicate the benzocyclopropenyl radical to be intermediate in stability to the cation and anion. The latter is charge delocalized and stabilized, while antiaromaticity, analogous to that exhibited by the cyclopropenyl anion, is not predicted.



4a **4b**

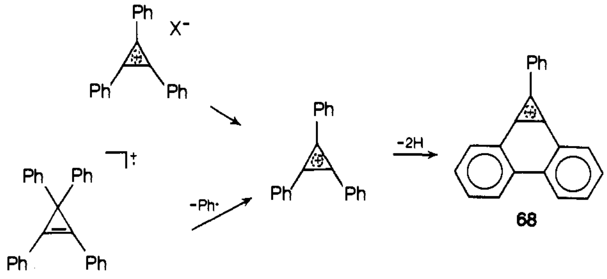
Positive Charge Distribution

Evidence for the existence of the benzocyclopropenyl cation comes from the mass spectral fragmentation of the benzocyclopropenes. Thus the base peak in the spectrum of the dichloro[11] derivative corresponds to the loss of a chlorine atom and the diester **35a** shows[20] a weak (11%) $[P - CO_2Me]^+$ ion. The dichloro compound does not undergo thermal rearrangement and therefore the [P − 35] species is reasonably postulated as the benzocyclopropenium ion. The proposal of the aromatic ion from the diester derivative is also reasonable because the mass spectrum of the rearranged compound shows no ion with significant abundance at [P − 59].



46, R = Cl; R^1 = H
35a, R = CO_2Me; R^1 = Ph

Phenanthrocyclopropenium ions, *e.g.*, **68**, have been proposed in the fragmentation of tetraarylcyclopropenes and triarylcyclopropenium ions.[66] These species arise by cyclodehydrogenation analogous to that observed in the photochemistry of these systems.[17]



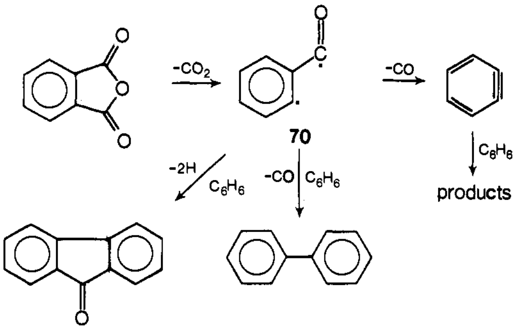
68

C. Benzocyclopropenones

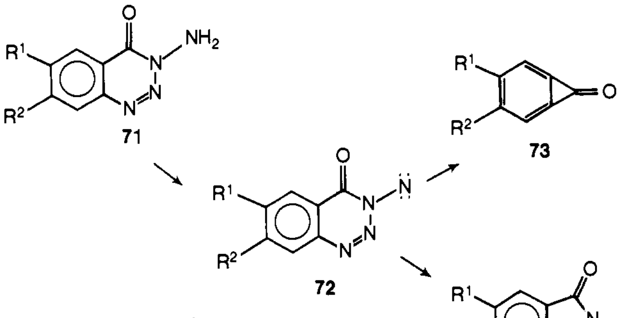
The ketone **69** derived from benzocyclopropene is expected[56] to be more stable than the parent ring system owing to charge separation and formation of an aromatic species, by analogy with the known aromaticity of the cyclopropenones. As yet, benzocyclopropenones have not been isolated, but there is little doubt that they, or species with the same symmetry, exist as transient intermediates in a variety of reactions.

69

The vapor-phase pyrolysis and electron impact induced decomposition of phthalic anhydride are consistent with the stepwise expulsion of carbon dioxide and carbon monoxide to produce dehydrobenzene.[67] Benzocyclopropenone, or more likely the "ring-open" species **70**, is a plausible intermediate in these processes. Similar results have been obtained from the mass spectral and pyrolytic decompositions of indantrione.[54]



The generation of species with the symmetry of benzocyclopropenones in solution is more recent and has been achieved by both thermal and photochemical reactions. The oxidation of a series of 3-aminobenzotriazin-4-ones (**71a–g**) with lead tetraacetate have been shown[55] to proceed by two simultaneous, but independent, routes to the benzocyclopropenones **73** and the indazolones **74**, respectively. The indazolones are formed by loss of 1 mol of nitrogen from the nitrene **72** and could be trapped in Diels-Alder reactions. Each of the indazolones gave rise to a single unrearranged benzoate ester with methanol. The benzocyclopropenones arise by the loss of 2 mol of nitrogen from the nitrene and the presence of species with this symmetry has been established by reaction with methanol. Isomeric pairs of methyl benzoates were isolated and, while the unrearranged esters could arise, at least in part, from the indazolones, the rearranged esters demand the intervention of a species with the symmetry



71 **72** **73** **74**

a, $R^1 = R^2$ = H
b, R^1 = Me; R^2 = H,
c, R^1 = H; R^2 = Cl
d, R^1 = Cl; R^2 = H
e, R^1 = H; $R^2 = NO_2$
f, $R^1 = NO_2$; R^2 = H
g, $R^1R^2 = C_6H_4$

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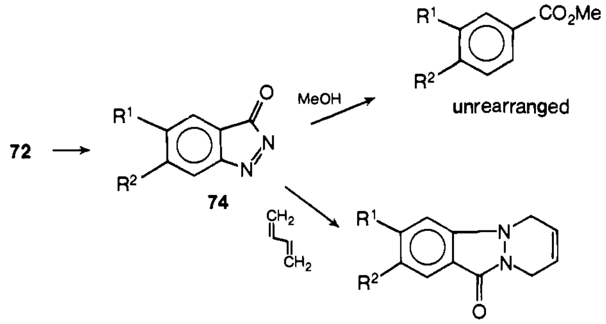
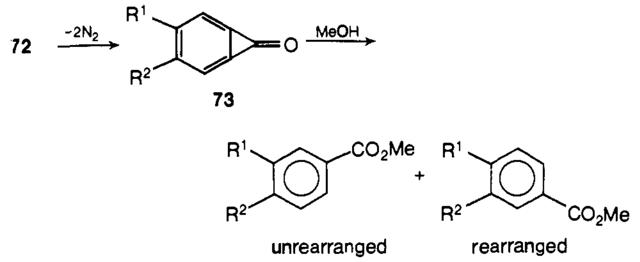
(66) M. A. Battiste and B. Halton, *Chem. Commun.*, 1368 (1968), and unpublished observations.

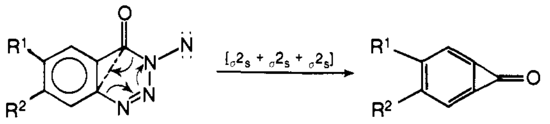
(67) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965).



of a benzocyclopropenone to account for the migration of the carbonyl group. The yields of rearranged esters (7–13%) thus provide a minimum estimate of the reaction which passes through the benzocyclopropenone. With **71g**, methyl naphthoate was obtained in 60% yield, and it can be presumed to arise, in part, from naphtho[*b*]cyclopropenone **(73g)**.

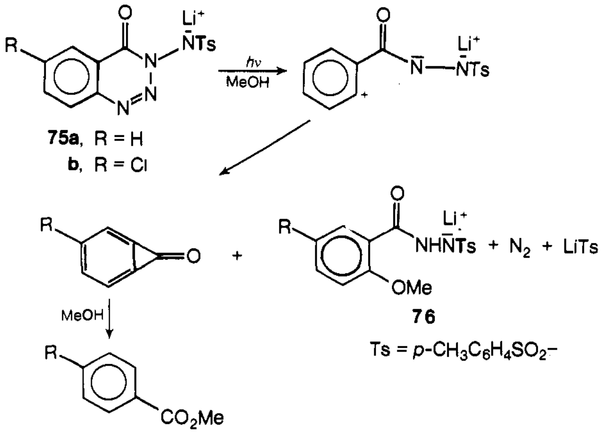


Orbital symmetry considerations[16] show that the benzocyclopropenones can be formed directly from **72** by an allowed $[_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$ pericyclic reaction. Furthermore, extended Hückel molecular orbital calculations on the "open" benzocyclopropenone show that the concerted loss of nitrogen from **72** is energetically feasable.

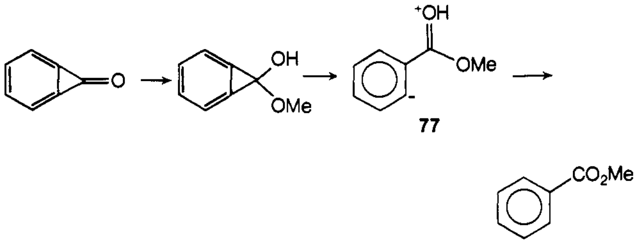


The formation of the indazolones is also allowed by symmetry arguments, either as a $[_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$ pericyclic reaction or as a $[_{\sigma}2_s + {}_{\sigma}2_a]$ process. However, it should be noted that elimination of nitrogen from the indazolones to give the benzocyclopropenones is forbidden.[55]

The photolysis of lithium 3-*p*-tolylsulfonylamino-1,2,3-benzotriazin-4-ones **(75)** also leads to benzocyclopropenones.[56] Irradiation of a methanolic solution of **75a** leads to methyl benzoate, lithium *p*-toluenesulfonate (LiTs), and o-methoxybenzoic acid *p*-toluenesulfonohydrazide **(76)**. With **75b**, methyl *p*-chlorobenzoate was the sole carboxylic ester isolated, thus demanding the intervention of the benzocyclopropenone. The formation of rearranged ester is consistent with inductive stabilization of developing carbanion character at the 1 position by the *m*-chlorine substituent.[2] However, the absence of methyl *m*-chlorobenzoate suggests that the unrearranged esters obtained in the oxidation route arise predominantly from the indazolones.



The ring cleavage of benzocyclopropenone has been suggested to proceed *via* the hemiacetal with a transition state close to **77** for the prototropic shift.[56] However, direct addition of solvent across the single bond, as discussed for the benzocyclopropenes, and proposed for the 1-aryl-2,3,3-trichlorocyclopropenes,[60] provides an alternative route.



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VI. Addendum

The first X-ray crystallographic structural analysis of a benzocyclopropene has now appeared. Dürr, *et al.*,[68] have examined dimethyl 1,4-diphenylbenzocyclopropene-7,7-dicarboxylate (**35b**) and found the bond lengths and bond angles (referred to Table I) to be a = 1.333, b = 1.387, c = 1.419, d = 1.392, e = 1.519 ± 0.008 Å; α = 126.5, β = 109.5, γ = 64.0 ± 0.5°. The three-membered ring was found to have the same parameters as cyclopropene[69] and to be out of plane with the aromatic ring by 1.5 ± 0.5°. The changes in bond lengths and angles caused by the fusion of the strained ring can only be viewed by comparison with *p*-terphenyl[70] which itself shows some bond length and angle deformations ($a = d$ = 1.407, b = c = 1.377 ± 0.005 Å; α = 121.8, β = 116.9 ± 0.3°).

From these results it is apparent that the benzocyclopropene exhibits some bond localization, but there is *no* evidence for this taking place either in the direction of the Longuet-Higgins–Coulson predictions (*viz.* **6**) or in the direction of the calculated geometry (*viz.* **2**). In fact, the observed geometry falls between both of these predictions with the 1–6 bond shortened to that of a normal cyclopropene as in **6** and the 2–3 and 4–5 bonds lengthened as in **2**. Consequently, the representation of benzocyclopropene by either of the Kekulé structures is erroneous.

The first derivative of the naphtho[*b*]cyclopropene ring system has now been characterized.[71] The *gem*-dichloro analog of **64** is obtained in 25% yield from the dehydro-

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(68) E. Carstensen-Oeser, B. Muller, and H. Dürr, *Angew. Chem.*, **84**, 434 (1972); *Angew. Chem., Int. Ed. Engl.*, 11, 422 (1972).

(69) H. M. Rietveld, E. N. Mason, and C. J. B. Clews, *Acta Crystallogr., Sect. B*, **26**, 693 (1970).

(70) J. D. Dunitz and V. J. Schomaker, *J. Chem. Phys.*, **20**, 1708 (1952); R. H. Kasai, R. J. Meyers, D. F. Eggers, and K. B. Wiberg, *ibid.*, **30**, 512 (1959).

(71) A. R. Browne and B. Halton, *J. Chem. Soc., Chem. Commun.*, *in press*.

chlorination of 1,6,7,7-tetrachloro-2,5-diphenylbenzo[3,4]-bicycloheptene in a manner strictly analogous to the synthesis of **46** (see section II.D). The compound shows an "aromatic double bond" stretching frequency at 1675 cm^{-1} in the infrared (KBr disk), and the base peak of the mass spectrum corresponds to the naphtho[*b*]cyclopropenyl cation arising by loss of a chlorine atom from the molecular ion. The chemistry of the naphthocyclopropene parallels that of the benzocyclopene analog **46.** For example, when treated with methanol the three-membered ring is cleaved and gives rise to methyl 1,4-diphenyl-2-naphthoate *via* the corresponding trimethyl ortho ester.