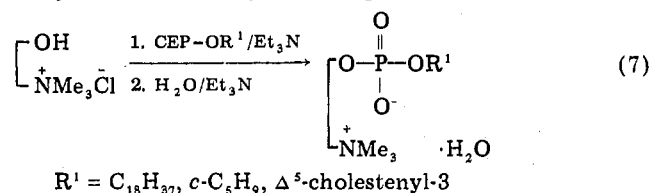


a crystalline monohydrate (eq 7).



Conclusions

Our basic three-step synthesis of phosphodiester is a practical route to complex and sensitive compounds of the type needed in studies of some biochemical processes at the molecular level. The neighboring-group effect involving *tert*-butyldimethylsilyl and phosphodiester functions could be particularly useful in the synthesis of ribopolynucleotides, and hence in the construction of transfer RNA fragments.^{4e} In this approach, the first nucleoside of the chain needs protection at 2'-OH and 5'-OH, the internal nucleosides

require protection only at 2'-OH, and the last nucleoside of the sequence may not require protection at all, since the terminal 3'-OH is not phosphorylated.

This research has also provided glimpses into the complexity of phosphorylation mechanisms, in particular the power of nucleophilic catalysis and the importance of aprotic media of relatively low polarity. In this respect, the work has extended our knowledge of related phenomena in aqueous media. It is possible that the intermediacy of pentacoordinate and hexacoordinate phosphorus species may be an important characteristic of enzymatic phosphorylations. The striking effects of imidazole, triethylamine, phenoxide ion, and acetate ion in our experiments provide models for the possible behavior of histidine, lysine, arginine, tyrosine, aspartic acid, and glutamic acid residues in enzymatic reactions. These amino acid residues are known to be involved in many phosphoryl-transfer active sites.

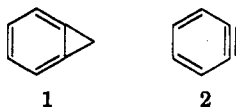
Synthesis and Chemistry of Benzocyclopropenes

W. EDWARD BILLUPS

Department of Chemistry, Rice University, Houston, Texas 77001

Received March 2, 1977

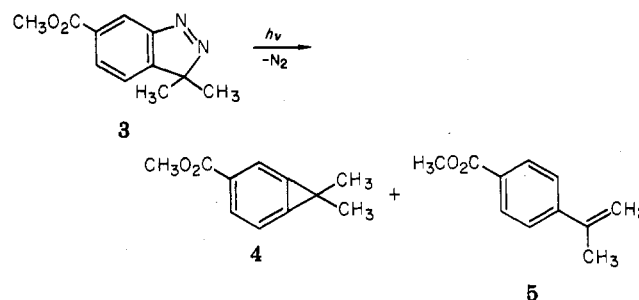
Benzocyclopropene (1) and benzyne (2) constitute the



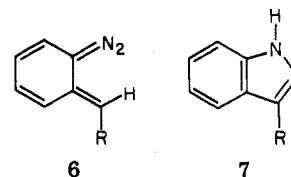
most highly strained members of the series of 1,2-bridged derivatives of benzene. Whereas benzyne is a transient species, detected only at low temperature using infrared spectroscopy of a matrix,¹ benzocyclopropene exhibits remarkable thermal stability despite the high strain energy associated with this ring system. In this Account, I will discuss some recent developments in benzocyclopropene chemistry, including synthesis and important physical and chemical properties of these fascinating hydrocarbons. The reader is referred to the excellent comprehensive review² by Halton in which earlier work in this field is described.

Synthesis

The first synthesis of a benzocyclopropene derivative was reported by Anet and Anet³ in 1964. They found that the 3*H*-indazole 3 underwent smooth elimination of molecular nitrogen upon photolysis with the formation of 4 in low yield along with methyl 4-isopropenylbenzoate (5). Closs⁴ utilized this route in the synthesis of several derivatives of benzocyclopropene



and has provided evidence for triplet diradical intermediates, although it is not clear whether they arise directly from the indazole or diazo compound 6. Since

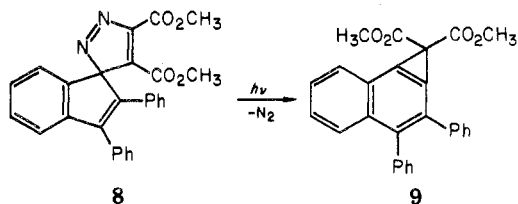


3-monosubstituted indazoles exist in the 1*H* form 7, this method is useful only for the synthesis of *gem*-disubstituted benzocyclopropenes.

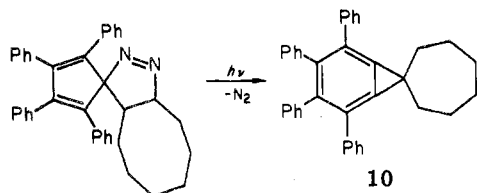
Dürr and Schrader⁵ prepared 9, the first naphthocyclopropene, in 30% yield by irradiation of the

W. E. Billups is Associate Professor of Chemistry at Rice University. He received the B.S. degree from Marshall University in 1961. This was followed by a period in industry with the Union Carbide Corporation. In 1968 he entered the graduate school of The Pennsylvania State University and received the Ph.D. in 1970. He then joined the Chemistry Department at Rice University. His research interests are divided among the areas of small-ring compounds, reactive intermediates, and organotransition-metal chemistry.

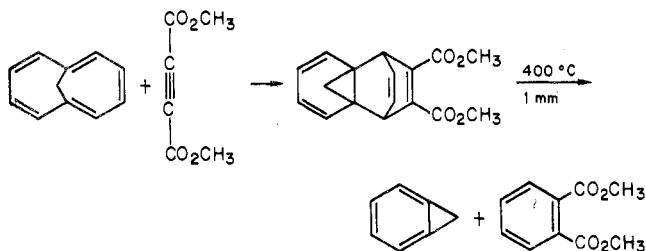
(1) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Am. Chem. Soc.*, **95**, 6134 (1973).
 (2) B. Halton, *Chem. Rev.*, **73**, 113 (1973).
 (3) R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).
 (4) G. L. Closs, *Adv. Alicycl. Chem.*, **1**, 53 (1966); G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Am. Chem. Soc.*, **89**, 3376 (1967).
 (5) H. Dürr and L. Schrader, *Angew. Chem.*, **81**, 426 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 446 (1969); *Chem. Ber.*, **103**, 1334 (1970).



spiro-3*H*-pyrazole **8**. Another application⁶ was the preparation of **10** in 30% yield, the only spirobenzocyclopropene that has been reported.



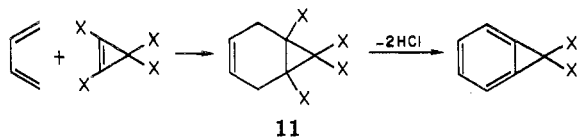
The elegant Diels–Alder, retro-Diels–Alder route illustrated below was used by Vogel and his co-workers⁷ in 1965 to prepare benzocyclopropene itself in 45%



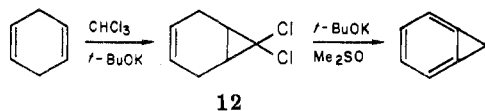
yield. This route is suitable for the preparation of various benzocyclopropenes which exhibit moderate thermal stability, but others do not survive the high reaction temperature.

More recent work at Cologne by Vogel and his co-workers⁸ and by Halton⁹ has demonstrated that bicyclo[4.1.0]heptenes are excellent precursors to benzocyclopropenes. These compounds are particularly attractive since they can usually be made in one step from commercially available starting materials and their conversion to benzocyclopropenes is easily effected in satisfactory yield.

In one approach the bicyclo[4.1.0]heptene **11** com-



mences with Diels–Alder addition of tetrahalocyclopropenes to 1,3-butadiene.¹⁰ Base-induced dehydrohalogenation leads directly to the benzocyclopropene.⁸ 7,7-Dichlorobicyclo[4.1.0]hept-3-ene (**12**), which is



prepared readily from dichlorocarbene and 1,4-cyclo-

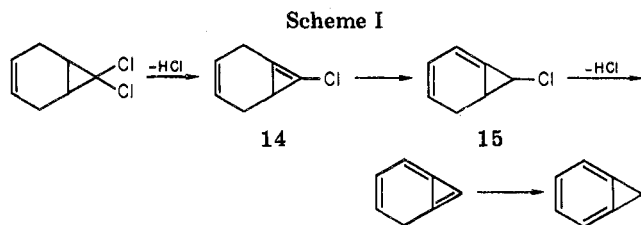
(6) H. Dürr and H. Schmitz, *Angew. Chem.*, **87**, 674 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 647 (1975).

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

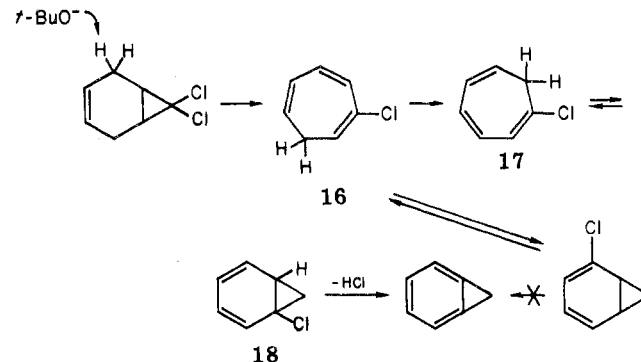
(8) E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem.*, **80**, 279 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 289 (1968).

(9) B. Halton and P. J. Milsom, *Chem. Commun.*, 814 (1971); A. R. Browne and B. Halton, *ibid.*, 1341 (1972).

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

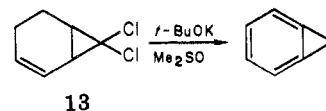


Scheme I



Scheme II

hexadiene,¹¹ yields the parent hydrocarbon in 40% yield upon treatment with potassium *tert*-butoxide (*t*-BuOK) in dimethyl sulfoxide.^{12,13} Bicyclo[4.1.0]hept-2-ene (**13**)

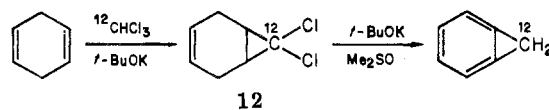


also yields benzocyclopropene in 20% yield.¹⁴

These reactions are clearly more complex than the simple dehydrohalogenations of the bicyclo[4.1.0]heptenes prepared from the Diels–Alder reaction. One possible pathway involves a series of base-induced elimination–isomerization reactions (Scheme I). Initial elimination of HCl gives the cyclopropene **14**, which rapidly undergoes double-bond isomerization, giving **15** after reprotonation. A second sequence of elimination–isomerization reactions gives benzocyclopropene.

Another route suggested by Halton² is illustrated in Scheme II. In this scheme, **12** is converted initially to **16**. A [1,5]-hydrogen shift would yield **17** which, under the reaction conditions, would be converted to benzocyclopropene by elimination of HCl from its valence tautomer **18**.

The labeling experiment of Prestien and Günther¹⁵ provides evidence in support of Scheme I. They prepared **12** from ¹²CHCl₃ and 1,4-cyclohexadiene and



found that the benzocyclopropene derived from this precursor retained the label at C-7 (absence of ¹³C nuclear magnetic resonance signal). A contribution

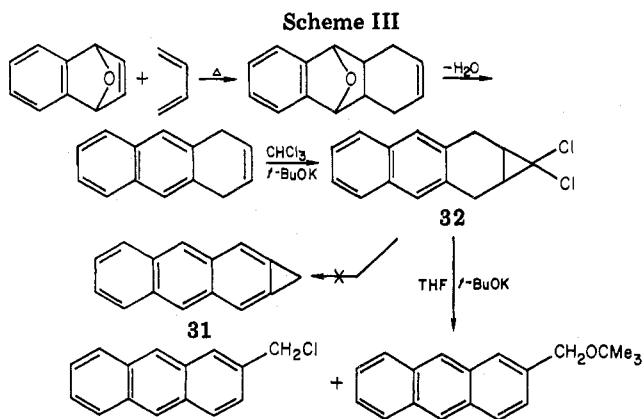
(11) P. S. Skell and S. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

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

(13) W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Org. Synth.*, **55**, 12 (1976).

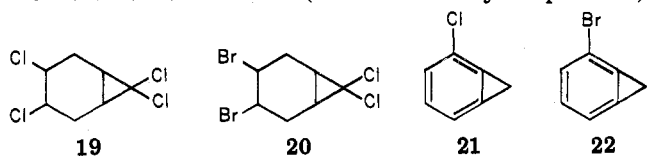
(14) W. Y. Chow, Ph.D. Thesis, Rice University, 1973.

(15) J. Prestien and H. Günther, *Angew. Chem.*, **7**, 985 (1974); *Angew. Chem. Int. Ed. Engl.*, **13**, 276 (1974).

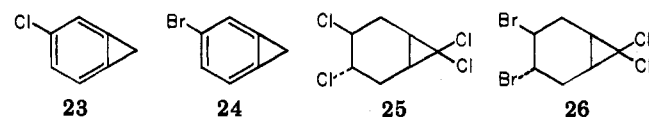


from the mechanism of Scheme II would require the presence of label at the bridging carbons.

The recent report of Devaprabhakara and co-workers¹⁶ that 19 and 20 (stereochemistry unspecified)

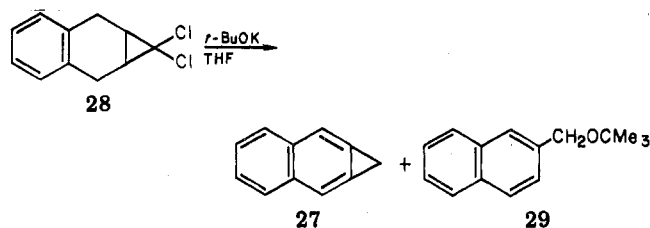


give benzocyclopropenes 21 and 22, respectively, via a mechanism similar to Scheme II when treated with $t\text{-BuOK}$ in Me_2SO has been shown to be incorrect. However, the functionalized benzocyclopropenes 23 and 24 have been prepared from 25 and 26, respectively,

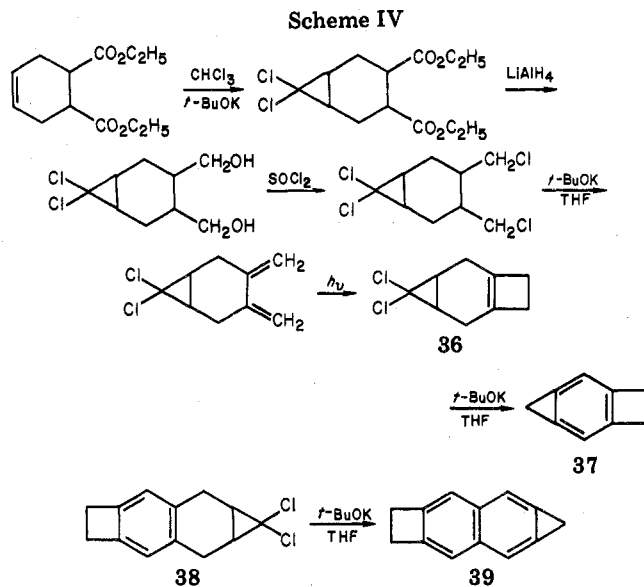
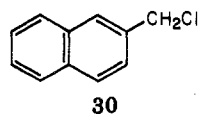


upon treatment with $t\text{-BuOK}$ in dimethyl sulfoxide.^{17,18}

Several additional applications of the *gem*-dichlorocyclopropane route¹² have been made recently. The parent hydrocarbon naphtho[b]cyclopropene (27)



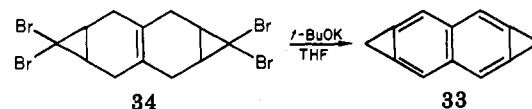
has been prepared in 65% yield along with the ether 29 by treating 28 with an eightfold excess of potassium *tert*-butoxide in tetrahydrofuran (THF).¹⁹ The yield of 27 is extremely sensitive to the concentration of potassium *tert*-butoxide.²⁰ Under some conditions the chloride 30 is also observed. It is interesting that, when



dimethyl sulfoxide is used as solvent under conditions identical with those employed in the synthesis of benzocyclopropene,¹² the yield of 27 is <10%.

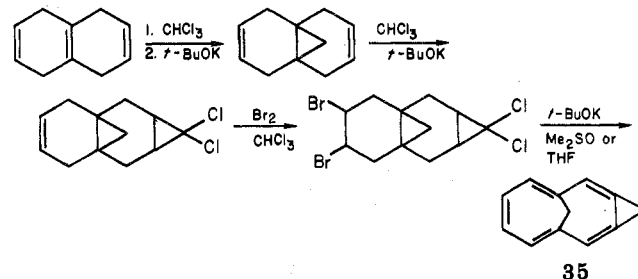
Curiously, it has not been possible to prepare anthro[b]cyclopropene (31) via the strictly analogous sequence of reactions outlined in Scheme III.²¹ The synthesis of the precursor 32 is uneventful; however, attempts to convert this compound to 31 under an expansive variety of conditions have failed. Although it is reasonable to postulate the formation of 31 as a reactive intermediate, various other routes also adequately account for the observed products. Additional evidence is required before a more definitive explanation can be put forward.

The fascinating compound, naphtho[b,e]biscyclopropene (33), results from dehydrobromination of 34.²²



The high strain energy of this hydrocarbon is manifested in a tendency for explosive decomposition.

Vogel and his co-workers²³ and Blakeney²⁴ have prepared 35, the first cyclopropene annelated with an



aromatic system other than benzene or naphthalene. Although some of the chemical properties of this molecule have been determined,²³ it does not exhibit the thermal stability of benzocyclopropene or the naphthocyclopropenes.

(16) A. Kumar, S. R. Tayal, and D. Devaprabhakara, *Tetrahedron Lett.*, 863 (1976).

(17) W. E. Billups, W. Y. Chamberlain, and M. Asim, *Tetrahedron Lett.*, 571 (1976).

(18) D. Davalian and P. J. Garratt, *Tetrahedron Lett.*, 4177 (1976).

(19) W. E. Billups and W. Y. Chow, *J. Am. Chem. Soc.*, 95, 4099 (1973).

(20) A. R. Browne, B. Halton, and C. W. Spangler, *Tetrahedron*, 30, 3289 (1974).

(21) W. E. Billups and M. Asim, unpublished observation; see also ref 26.

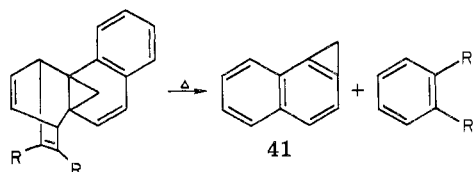
(22) J. Ippen and E. Vogel, *Angew. Chem.*, 86, 780 (1974); *Angew. Chem. Int. Ed. Engl.*, 13, 736 (1974).

(23) E. Vogel and J. Sombrock, *Tetrahedron Lett.*, 1267 (1974).

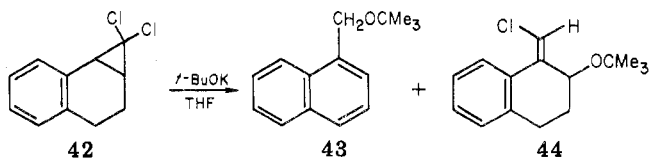
(24) A. J. Blakeney, Ph.D. Thesis, Rice University, 1976.

The novel benzocyclopropene **37** in which benzene is fused to both a three- and a four-membered ring has been prepared by Davalian and Garratt²⁵ in the skillful approach outlined in Scheme IV. Treatment of **36** with *t*-BuOK in THF gave **37**, in 30–40% yield. Similarly, **38** gives **39** in 46% yield.²⁶

The parent hydrocarbon, naphtho[*a*]cyclopropene (**41**), is not accessible from the *gem*-dichlorocyclo-

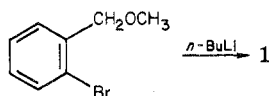


propane route,²⁷ although it was prepared²⁸ recently by the retro-Diels-Alder reaction illustrated. When **42** is

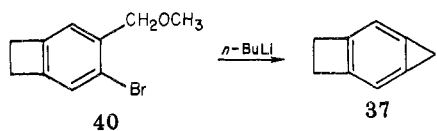


treated with *t*-BuOK in THF under conditions which give naphtho[*b*]cyclopropene from **28**, compounds **43** and **44** (provisionally identified) are the major products, along with other minor unidentified compounds. The failure to obtain **41** is not unexpected in view of the proposed mechanism (Scheme I) which requires high-energy cyclopropenyl anion intermediates. It thus appears that the *gem*-dichlorocyclopropane route¹² to benzocyclopropenes is useful only for linearly fused derivatives.

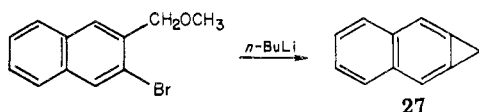
The preparation of benzocyclopropene in 35% yield



from bromobenzyl methyl ether and *n*-butyllithium (method of Radlick)²⁹ is the most recent synthesis of this hydrocarbon. Unfortunately, applications of this method to the synthesis of other benzocyclopropenes have been somewhat disappointing. Compound **37** has



been prepared³⁰ in 5% yield from **40**, whereas a faint odor of **27** results from the reaction of **41** with *n*-bu-



tyllithium.²⁷ The odor (foul) of **27** (or **1**) would allow sensual detection reliably at 10⁻⁴ %.

(25) D. Davalian and P. J. Garratt, *J. Am. Chem. Soc.*, **97**, 6883 (1975).

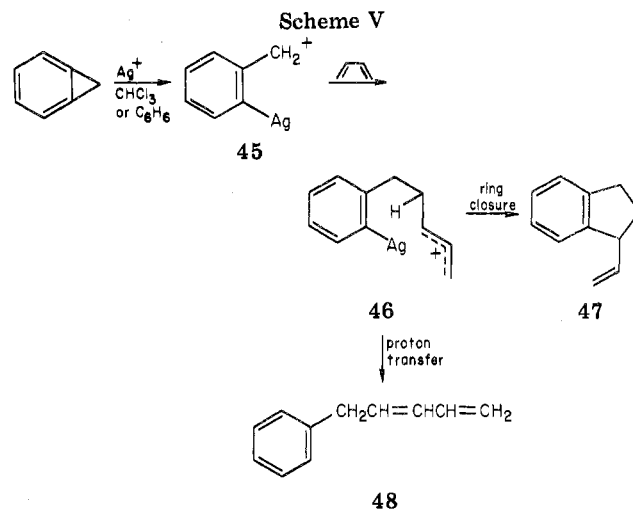
(26) D. Davalian and P. J. Garratt, *Tetrahedron Lett.*, 2815 (1976).

(27) W. E. Billups and L. E. Reed, unpublished observation.

(28) S. Tanimoto, R. Schafer, J. Ippen, and E. Vogel, *Angew. Chem.*, **15**, 613 (1976); *Angew. Chem., Int. Ed. Engl.*, **88**, 643 (1976).

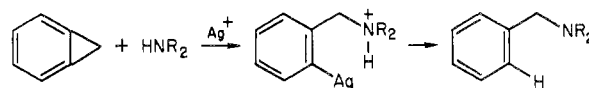
(29) P. Radlick and H. T. Crawford, *Chem. Commun.*, 127 (1974).

(30) C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 4539 (1975).



Chemistry of Benzocyclopropenes

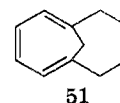
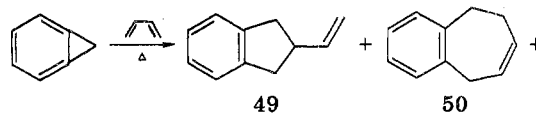
Under catalysis by silver ion, benzocyclopropene is a benzylating reagent par excellence.³¹ Alcohols, mercaptans, and amines all react with benzocyclopropene at 0 °C in aprotic solvents to yield the benzylated product. A plausible scheme which has precedent in the reactions of other strained ring systems with silver ion³¹ is illustrated below in the reaction of benzocyclopropene with a secondary amine.



These reactions can also be effected thermally at 100 °C. It is tempting to postulate diradical intermediates in the thermally initiated reactions; however, the production of benzylamines from the reaction is clearly inconsistent with such a mechanism, since hydrogen atom abstraction at carbon rather than nitrogen would be expected. The thermally induced reactions may be catalyzed by the glass reaction vessel. Alternatively, they may result from nucleophilic addition on the strained ring.

Silver ion also catalyzes some reactions of benzocyclopropene with other reagents, including olefins, dienes, allenes, and acetylenes.³² An example is the extremely facile reaction of benzocyclopropene with butadiene (Scheme V). It seems reasonable to invoke **45** and **46** as intermediates in this process. The observed products **47** and **48** would arise directly from intermediate **46** via ring closure and proton transfer, respectively.

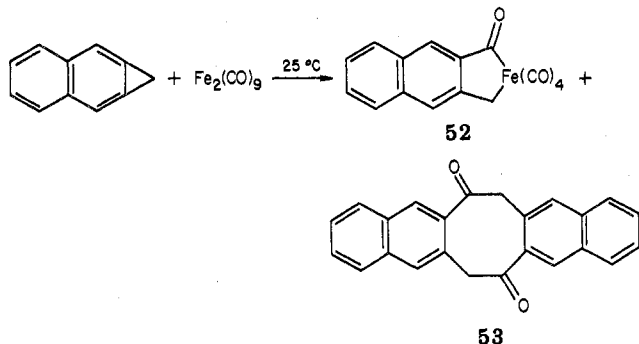
The silver ion catalyzed reaction of Scheme V stands in contrast with the thermally induced reaction of benzocyclopropene and butadiene which yields products **49–51**,³³ probably from diradical intermediates.



(31) W. E. Billups, W. Y. Chow, D. Wolf, and C. V. Smith, unpublished observation.

(32) W. E. Billups, W. Y. Chow, and C. V. Smith, *J. Am. Chem. Soc.*, **96**, 1979 (1974).

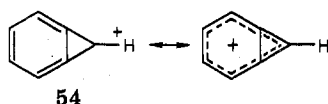
In the expectation that partial bond localization in benzocyclopropene might lead to interesting π complexes with metal carbonyls, the reactions of benzocyclopropene and naphtho[*b*]cyclopropene with $\text{Fe}_2(\text{CO})_9$ were investigated. With benzocyclopropene only intractable materials were obtained; however, naphtho[*b*]cyclopropene and $\text{Fe}_2(\text{CO})_9$ give the stable heterocycle **52** in 27% yield, along with a trace of the



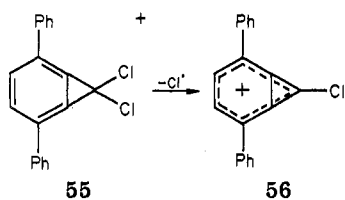
diketone **53**.³⁴ Other products were also produced, but structural characterization was not possible. Complete structural characterization of **52** was accomplished by X-ray single-crystal analysis.³⁴ The thermal stability of **52** is probably kinetic in origin, since metal alkyl decomposition pathways such as carbon-carbon bond reorganization or β elimination are not available. It is interesting that structures similar to **52** have been proposed, but not characterized, by Collman and his co-workers as intermediates in the synthesis of aliphatic ketones from $\text{Na}_2\text{Fe}(\text{CO})_4$ and alkyl halides.^{35,36}

The Benzocyclopropenyl Cation, Radical, and Anion

Although the benzocyclopropenyl cation (**54**) received



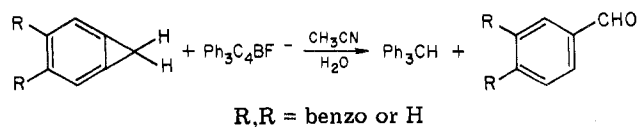
theoretical attention as early as 1952,³⁷ the only evidence until quite recently for the existence of such an ion was from the mass spectral fragmentation of substituted benzocyclopropenes.^{2,5} For instance, **55** shows



a P - 35 peak which is reasonably postulated as the benzocyclopropenium ion **56**.

The parent benzocyclopropenium ion and some of its derivatives have been generated in solution. Thus both benzocyclopropene³⁸ and naphtho[*b*]cyclopropene³⁹

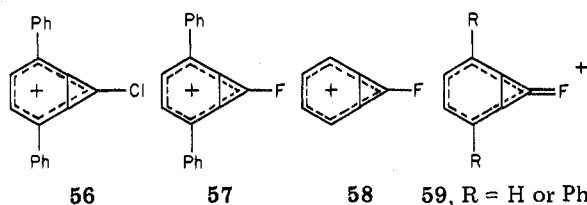
react with trityl fluoroborate in acetonitrile to yield, in addition to triphenylmethane, benzaldehyde and β -naphthylaldehyde, respectively, after hydrolysis of the



R,R = benzo or H

reaction mixture. These results can be taken as evidence for the formation of the respective cations.

A recent report describes the direct observation of cations **56**, **57**, and **58** by ^{13}C NMR spectroscopy.⁴⁰ Ions

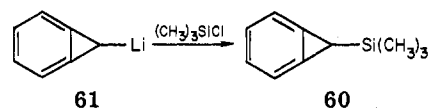


57 and **58** appear to derive significant stabilization from structure **59**. In all cases the empirical charge density distributions were found to be in qualitative agreement with SCC-EH MO (self-consistent charge-extended Hückel molecular orbital) calculations for the parent benzocyclopropenium ion.⁴¹ Ion **56** has also been isolated as the unstable hexachloroantimonate salt. Although these data provide overwhelming evidence for the discrete existence of benzocyclopropenium ions, a complete NMR spectroscopic analysis of the parent benzocyclopropenium ion would be welcome.

The benzocyclopropenyl radical⁴¹ has been predicted to be intermediate in stability between that of the cation and anion. Experimental evidence in support of this prediction is not available.

The anion⁴¹ is predicted to be less stable than either benzocyclopropene itself or the cation, although possibly more stable than the parent cyclopropenyl anion by virtue of delocalization. Simple Hückel MO theory (which neglects distortion of the aromatic ring) indicates that the anion has a slightly lower total energy than the benzyl anion.

The remarkable success of Eaborn and co-workers⁴² in achieving the synthesis of **60** from the lithio deriv-



ative **61** implies that benzocyclopropene is acidic. In fact, **60** is cleaved by sodium hydroxide at 50°C approximately 64 times as rapidly as benzyltrimethylsilane, giving a $\text{p}K_a$ of ~ 36 for benzocyclopropene.

Bond Fixation, Strain Energy, and Spectroscopy

The concept of bond fixation, which was first advanced by Mills and Nixon⁴³ in 1930, has been under

(33) S. Korte, Ph.D. Thesis, University of Cologne, 1968, as read in ref 2.

(34) F. A. Cotton, J. M. Troup, W. E. Billups, L. P. Lin, and C. V. Smith, *J. Organometal. Chem.*, **102**, 345 (1975).

(35) J. P. Collman, S. R. Winter and D. R. Clark, *J. Am. Chem. Soc.*, **94**, 1788 (1972); W. O. Siegl and J. P. Collman, *ibid.*, **94**, 2516 (1972).

(36) M. P. Cooke, Jr., *J. Am. Chem. Soc.*, **92**, 7080 (1970).

(37) J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(38) P. Müller, *Helv. Chim. Acta*, **56**, 500 (1973).

(39) W. E. Billups and W. Y. Chow, unpublished observation.

(40) B. Halton, H. M. Hugel, D. P. Kelly, P. Müller, and U. Burger, *J. Chem. Soc., Perkin Trans. 2*, 258 (1976).

(41) B. Halton and M. P. Halton, *Tetrahedron*, **29**, 1717 (1973).

(42) C. Eaborn, R. Eidenschink, S. J. Harris, and D. R. M. Walton, *J. Organometal. Chem.*, **C27**, 124 (1977).

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

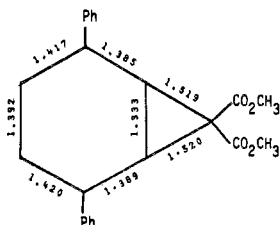


Figure 1. Bond lengths of dimethyl 2,5-diphenylbenzocyclopropene-1,1-dicarboxylate.

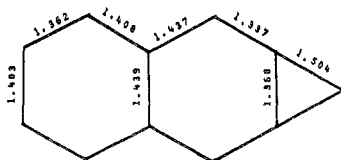
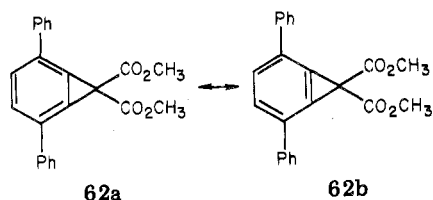


Figure 2. Bond lengths of naphtho[b]cyclopropene.

active investigation in recent years. Although the early work of Mills and Nixon has been subjected to reinterpretation,⁴⁴ the effect is still frequently used to denote nonequivalence of bonds in benzene resulting from annelation. Such an effect would be particularly pronounced with the highly strained 1,2-bridged systems benzyne and benzocyclopropene, but probably to a much lesser extent with benzocyclobutene and other benzocycloalkenes.

X-ray crystallographic data, and thus exact bond lengths, are available for two benzocyclopropenes. Carstensen-Oeser, Müller, and Dürr⁴⁵ examined dimethyl 1,4-diphenylbenzocyclopropene-7,7-dicarboxylate (**62**) and found the bond lengths shown in Figure 1. It is apparent from these data that some bond localization exists; however, the striking feature is the absence of bond localization exactly in accordance with either Kekule structure **62a** or **62b**. The shortened 1,6



bond may result from the ester substituents at C-7, analogous to other electron-withdrawing substituents which stabilize norcaradiene structures relative to cycloheptatrienes.⁴⁶ One might also argue that the bridging bond is compressed by the bridging group. The X-ray data for naphtho[b]cyclopropene⁴⁷ (Figure 2) show the same anomalies, but differ from the previous case by less extreme shortening of the bridging bond.

The first experimentally derived strain energy of benzocyclopropene was determined in 1973⁴⁷ from a study of the heats of the silver ion catalyzed solvolyses discussed earlier. The enthalpy of the silver ion catalyzed methanolysis of benzocyclopropene, which is rapid at room temperature, was determined to be -49.4

± 0.2 kcal mol⁻¹ at 25 °C. The enthalpy of solution of the product benzyl methyl ether in methanol was also determined (0.70 ± 0.02 kcal mol⁻¹), so that the heat of reaction with all components in the liquid state could be obtained. To evaluate the strain it was necessary to compare the experimentally determined heat of formation with a value from a strain-free model. The heat of formation of benzyl methyl ether had never been measured, but was approximated from Franklin's group equivalents⁴⁸ as $+17.38$ kcal mol⁻¹. The strain in benzocyclopropene is calculated from these data to be 68 kcal mol⁻¹. This value is substantially greater than the total strain energy of 52.6 kcal mol⁻¹ found for cyclopropene and is comparable to the value of 68.2 kcal mol⁻¹ reported by Turner⁴⁹ for 1,3-dimethylbicyclo[1.1.0]butane, although two bonds are broken in the bicyclobutane, whereas only one bond is broken in benzocyclopropene.

The strain energy of naphtho[b]cyclopropene derived from the methanolysis reaction is 65–67 kcal mol⁻¹. Combustion calorimetry gives 67 kcal mol⁻¹, confirming the value obtained from the methanolysis study, and, as expected, not appreciably different from that found for benzocyclopropene.

Some combustion data for **33** are now available, and a strain energy of 166 kcal mol⁻¹ has been determined.⁵⁰ It should be emphasized, however, that this represents a lower limit for the strain energy of this compound, since it was extremely difficult to achieve clean combustion of this "energy-rich" molecule. It is interesting that the strain energy of **33** exceeds that found for naphtho[b]cyclopropene by more than a factor or two. The additional 33–35 kcal would arise from excessive distortion induced by the presence of two three-membered rings.

The ¹H NMR spectra of benzocyclopropenes reveal fairly normal chemical shifts. For example, the protons of the central ring in naphtho[a]cyclopropene and naphtho[b]cyclopropene reside in the range for aromatic protons.^{19,30}

The ¹³C NMR spectra of several benzocycloalkenes including benzocyclopropene have been discussed recently in terms of ring strain.⁵¹ The ¹³C chemical shifts of benzocyclopropenes, benzocyclobutene, indan, and *o*-xylene are shown in Table I. It is clear from these data that strain has an effect on chemical shift, especially at C-3 (or C-6) where increasing strain is associated with increased shielding from 130 ppm for *o*-xylene to 114.7 ppm for benzocyclopropene. The picture at C-1 (or C-2) is somewhat more puzzling. Benzocyclopropene is shielded substantially at these positions, whereas the chemical shifts of the remaining entries in Table I suggest that increased strain is associated with deshielding. The shielding of C-1 in benzocyclopropenes is probably associated with the special nature of the cyclopropyl ring system which is known to experience shielding. The remaining aromatic carbons (C-4 and C-5) span a range of only 2.8 ppm on going from *o*-xylene to benzocyclopropene, indicating that these positions are not very sensitive to strain.

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

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

(46) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454 (1967).

(47) W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness, and J. L. Wood, *J. Am. Chem. Soc.*, **95**, 7878 (1973).





(48) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).

(49) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).

(50) F. D. Rossini and W. E. Billups, unpublished observation.

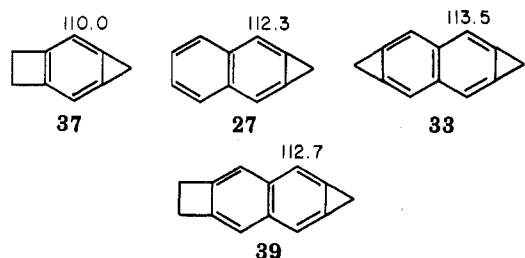
(51) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, **41**, 751 (1976).

Table I
¹³C NMR Assignments of Benzocyclopropene,^a Benzocyclobutene, Indan, and *o*-Xylene^{b,c}

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Aliphatic carbons	
							α	β
	125.4	125.4	114.7	128.8	128.8	114.7	18.4	
	145.6	145.6	122.1	126.6	126.6	122.1	29.4	
	144.0	144.0	124.4	126.2	126.2	124.4	33.8	25.4
	136.3	136.3	129.8	126.0	126.0	129.8	19.4	

^a The numbering scheme used here is consistent with that used for other benzocycloalkenes. The system devised by Halton² and used elsewhere^{16,17} represents benzocyclopropene as a bond-fixed structure. ^b Data taken from ref 51. ^c δ values.

Since the data of Table I suggest that strain exerts the greatest effect on the chemical shifts of carbons at C-3 and C-6, it is interesting to compare the ¹³C chemical shifts of these carbons in compounds **37**, **27**, **33**, and **39**. Compound **37** is probably the most highly



strained member of the benzocyclopropene family that has been reported and, as expected, experiences the greatest shielding at these positions. However, the naphthocyclopropenes fall in a narrow range, suggesting that the use of ¹³C chemical may not provide a reliable method of ranking such compounds with regard to strain.

The infrared spectra of benzocyclopropenes exhibit a characteristic band around 1670 cm⁻¹ thought to arise from a stretching vibration. This band is commonly referred to as an "aromatic double bond". For benzocyclopropene this absorption appears at 1666 cm⁻¹ and for naphtho[*b*]cyclopropene at 1673 cm⁻¹. Otherwise, infrared spectra of benzocyclopropenes are simple, indicating the high degree of symmetry in these molecules.

The ultraviolet spectra of the more highly strained benzocyclopropenes such as **37** exhibit strain-related bathochromic shifts when compared to benzocyclopropene. Benzocyclopropene itself does not differ appreciably from benzene, which suggests that the aromatic chromophore is not disrupted appreciably.

I am indebted to my co-workers, whose names appear in the literature cited. The research has been supported by The Robert A. Welch Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, and Eli Lilly and Company. A fellowship from the Alfred P. Sloan Foundation is also gratefully acknowledged.

Chemistry of Multilayered Cyclophanes

SOICHI MISUMI* and TETSUO OTSUBO

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

Received September 28, 1977

When two or more aromatic rings are stacked face to face, some transannular interaction is expected between their π -electronic systems. Such an interaction has been, in fact, observed in studies on many double-

Soichi Misumi is Professor of Organic Chemistry at Osaka University. He received his Ph.D. degree from Osaka University for work on conjugated polyene and polyyne systems with Masazumi Nakagawa and joined the staff of the Institute of Scientific and Industrial Research in 1966.

Tetsuo Otsubo received both his M.S. and his Ph.D. (in 1972) degrees from Osaka University and then spent 2 years as postdoctoral fellow at the University of Oregon with V. Boekelheide. Both authors are interested in the study of syntheses and intramolecular interactions of layered aromatic compounds and exciplexes.

layered compounds, such as [2.2]paracyclophane (**1**), other cyclophanes, helicenes,¹ and janusenes.²

Unusual molecular deformation or strain is brought about by π -electron repulsion when the aromatic rings are closely fixed within van der Waals distance by virtue of short methylene bridges. For example, in [2.2]-paracyclophane (**1**) the two benzene rings are bent into a boat shape.³ Because of these structural features,

(1) R. H. Martin, *Angew. Chem.*, **86**, 727 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 649 (1974); R. H. Martin and M. Baes, *Tetrahedron*, **31**, 2135 (1975).

(2) S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, **89**, 1476 (1967).