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SYNTHESIS AND CHEMISTRY OF SUBSTITUTED BENZOCYCLOPROPENES

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Ph.D.  
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SYNTHESIS AND CHEMISTRY
OF SUBSTITUTED
BENZOCYCLOPROPENES

by

WAYNE A. RODIN

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

W. E. Billups, Professor of Chemistry, Chairman

K. H. Whitmire, Assistant Professor of Chemistry

L. V. McIntire, Professor of Chemical Engineering

Houston, Texas

May, 1986
Synthesis and Chemistry of Substituted Benzocyclopropenes

by

Wayne A. Rodin

Abstract

1H-Cyclopropa[b]phenanthrene \(33\) was synthesized in 89\% yield by dehydrohalogenation of 1a-bromo-9a-chloro-1a,2,9,9a-tetrahydro-1H-cyclopropa[b]phenanthrene \(43\) with potassium t-butoxide in THF at -20\°C. A key step in the synthesis of \(33\) was the Diels-Alder reaction of 1-bromo-2-chlorocyclopropene \(38\) with 1,2-dimethylene-1,2,3,5,6,7,8,9-octahydronaphthalene \(41\). The compound did not exhibit any unusual spectral properties. 1,2-Dihydrocyclobuta[b]phenanthrene \(49\) was also synthesized via the cycloaddition of \(41\) with dimethyl cyclobutene-1,2-dicarboxylate.

Cycloproparenes incorporating a second ring fusion were prepared via the Diels-Alder reaction of \(38\) with various dienes, followed by dehydrohalogenation of the Diels-Alder adducts with potassium t-butoxide. This method permitted the synthesis of the symmetrically annelated 3,4,5-trihydro-1H-cycloprop[f]indene \(67\) and 3,4,5,6-tetrahydro-1H-cyclopropa[b]naphthalene \(69\), as well as the asymmetrically annelated compounds 4,5,6-trihydro-
1H-cycloprop[e]indene 71 and 4,5,6,7-tetrahydro-1H-cyclopropa[a]naphthalene 73.

The nonlinearly fused cycloproparenes 71 and 73 were treated with several electrophiles to determine the degree of regioselectivity of cleavage of the three-membered ring. Compound 71, containing the five-membered second ring annelation, was highly regioselective with most electrophiles, giving either the alpha- or beta-substituted indans. Compound 73, containing the six-membered second ring fusion, gave a mixture of alpha- and beta-substituted tetrалins with all reagents. The high regioselectivity of 64 has been attributed to rehybridization of the orbitals due to the additional strain imposed by the second ring fusion.
ACKNOWLEDGEMENTS

I would like to thank Dr. W. E. Billups for his inspiration and guidance during my years as a graduate student. I would also like to thank my fellow graduate students for their friendship and assistance during the course of my research.

I wish to acknowledge the financial support provided by the Robert A. Welch Foundation in the form of a Predoctoral Fellowship, and the Gulf Oil Foundation for a Graduate Research Fellowship.
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This dissertation serves several purposes. The field of cyclopropaprene chemistry has been an active area of research for several years, and should continue to be so. Three compounds, in particular, have had a great deal of impact on the course of my graduate research: 1H-cycloprop[b]anthracene, cyclopropa[3,4]benzocyclobutene, and 1-bromo-2-chlorocyclopropene.

The first purpose of this work is to describe the synthesis of 1H-cyclopropa[b]phenanthrene, which is only the second parent cyclopropaprene higher than the naphthalene series to be reported. The synthesis of 1H-cycloprop[b]anthracene demonstrated that the higher homolog benzocyclopropene derivatives could be prepared, and provided the impetus for my work towards 1H-cyclopropa[b]phenanthrene and my unsuccessful work towards 1H,5H-biscycloprop[b,i]anthracene.

The second purpose of this work is to report the synthesis of a series of aneled benzocyclopropenes. Only two such compounds had been reported, cyclopropa[3,4]benzocyclobutene and cyclopropa[4,5]benzocyclobutene (60 and 29), which incorporate a four-membered ring fusion to the benzocyclopropene nucleus. We have prepared 3,4,5-trihydro-1H-cycloprop[f]indene and 4,5,6-trihydro-1H-cycloprop[e]indene, which incorporate the five-membered ring fusion, and 3,4,5,6-tetrahydro-1H-
cyclopropa[b]naphthalene and 4,5,6,7-tetrahydro-1H-cyclopropa[a]naphthalene, which incorporate the six-membered ring fusion.

The third purpose of this work is to explore the regioselectivity of the reactions of asymmetrically fused cycloproparenes with various electrophiles. The reaction of the asymmetrically fused cyclopropa[3.4]benzo-cyclobutene with electrophiles had been conducted by Garratt and was shown to be highly selective. We chose to investigate similar reactions with the asymmetrically fused compounds 4,5,6-trihydro-1H-cycloprop[e]indene and 4,5,6,7-tetrahydro-1H-cyclopropa[a]naphthalene.

Our fourth purpose in conducting this research is more general in scope, which is to demonstrate the general utility of 1-bromo-2-chlorocyclopropene as a cycloproparene synthon. Indeed, without this synthon, the structure and content of this dissertation would be considerably altered.
This dissertation is dedicated to Marvin. I apologize for the inconvenience.
SYNTHESIS AND CHEMISTRY
OF SUBSTITUTED
BENZOCYCLOPROPENES
INTRODUCTION

Strained aromatic systems have long fascinated organic chemists. Cycloproparenes, aromatic compounds incorporating the 1,2-methylene fusion, have been of particular interest[1]. These compounds exhibit unusual stability, in spite of the strain energy of the small ring annelation. A variety of cycloproparenes have been synthesized and studied to determine the amount of strain and distortion which can be incorporated in the aromatic nucleus. The strain energies of some representative cycloproparenes are given in Table I.

The concept of bond fixation, the localization of the "double bonds" of benzene, advanced by Mills and Nixon[4] in 1930, has been an active area of investigation in past years. A theoretical study[5] of the bond lengths and angles of indan and tetralin led to the conclusion that bond localization in annelated benzenes should appear as depicted in 4, and that the effect should be more pronounced in the benzocyclobutenes and -propenes [6].

X-ray crystallographic data are available for some cycloproparenes, providing accurate bond lengths and angles. These data are presented in Table II. The data
Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Strain Energy (Kcal/mol)</th>
<th>Ref.</th>
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<tr>
<td>1</td>
<td>68</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>67</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>166</td>
<td>3</td>
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Table II
(Bond Lengths)

<table>
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<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>Ref.</th>
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<td>1.368</td>
<td>1.337</td>
<td>1.437</td>
<td>1.439</td>
<td>1.504</td>
<td>2</td>
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<tr>
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<td>1.385</td>
<td>1.417</td>
<td>1.392</td>
<td>1.519</td>
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<tr>
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<td>1.355</td>
<td>1.423</td>
<td>1.411</td>
<td>1.52</td>
<td>9</td>
</tr>
</tbody>
</table>

The numbers in parentheses denote the b', c', and e' bond lengths.
indicate that some bond localization does occur, but it is remarkable that bond fixation is not in accordance with either Kekule structure $\text{la}$ or $\text{lb}$; instead, three adjacent short bonds are found ($b$-$a$-$b'$).

The bridge bond ($a$) is shorter than benzene (1.395 Å) and intermediate between cyclopropene (1.296 Å) and cyclopropane (1.510 Å). The effect is most pronounced in the geminally-disubstituted compounds, and is less extreme in the unsubstituted cyclopropa[b]naphthalene.

The first synthesis of a benzo[cyclopropene] was reported in 1964, with the isolation of $\text{8}$ by Anet and Anet (eq. 1) [10]. The 3H-indazole $\text{9}$ eliminated nitrogen when photolyzed, with formation of $\text{8}$ in low yield.

This route has been employed successfully by Closs [11] in the synthesis of gem-disubstituted cyclopropaprene; however, the method cannot be applied to mono- or unsubsti nated cyclopropaprene, since the 3H-indazole tautomerizes readily to the 1H form $\text{10}$. This restriction
has resulted in reduced interest in the 3H-indazole route.

A substituted cyclopropanaphthalene was prepared by Dürr and Schrader[12] utilizing the spiro-3H-pyrazole 11. Irradiation of 11 gave the substituted cyclopropanaphthalene 12 (eq. 2).

A similar approach led to the synthesis of the novel spirobenzocyclopropene 13 (eq. 3) [13].

A non-photochemical route to the cycloproparenes was developed by Vogel and used to synthesize benzocyclopropene
itself (eq. 4), via a retro-Diels-Alder reaction[14].

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} \\
\end{array}
\xrightarrow{\Delta}
\begin{array}{c}
\text{1} \\
\end{array}
\text{ (eq. 4)}
\]

This elegant route has also been used in the synthesis of 1H-cyclopropa[a]naphthalene (14) [15].

14

One of the more commonly utilized routes to cycloproparenes uses halogenated bicyclo[4.1.0]heptenes such as 15 and 16. In one approach, the compounds are

\[
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{X} \\
\text{X} \\
\end{array}
\quad
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{X} \\
\text{X} \\
\end{array}
\]

15 16

prepared via the Diels-Alder addition of 1,3-dienes to tetrahalocyclopropenes [16]. As indicated in Scheme I, base-induced dehydrohalogenation of the Diels-Alder adduct gives the 7,7-dihalobenzocyclopropene 17 [17].

Scheme I

\[
\begin{array}{c}
\text{C} = \text{C} \\
\text{X} \\
\text{X} \\
\text{X} \\
\end{array}
\begin{array}{c}
\text{X} \\
\text{X} \\
\end{array}
\xrightarrow{}
\begin{array}{c}
\text{X} \\
\text{X} \\
\end{array}
\begin{array}{c}
\text{X} \\
\text{X} \\
\end{array}
\begin{array}{c}
\text{17} \\
\end{array}
\]

The method has also been extended to the naphthalene derivative 18 [18].

A second route utilizes halogenated bicyclo[4.1.0]heptenes that are derived from the addition of dichlorocarbene to a cyclohexadiene. Benzocyclopropene itself can be synthesized on a preparative scale from 7,7-dichlorobicyclo[4.1.0]heptene 19 (eq. 5) [19].

The reaction is clearly more complex than the simple dehydrohalogenations of the compounds prepared via the Diels-Alder route. One possible pathway involves a series of base-induced elimination/isomerization reactions, as outlined in Scheme II. Evidence for this mechanism has been provided by labelling studies [20].
Scheme II

Unsaturation in the bicyclic precursor is not necessary if sufficient leaving groups are present. Thus the tetrahalobicyclohexanes 20 and 21 afforded the respective 3-halobenzocyclopropenes 22 and 23 [21].

The gem-dichloro route has been applied by chemists to several other cycloproparenes, although the preparation of the precursors rapidly becomes more involved. 1H-Cyclopropa[b]naphthalene can be isolated in 65% yield as a rather stable crystalline solid from the benzo derivative 24 (eq. 6) [22].
The gem-dichlorocyclopropane route has also been applied to non-benzenoid aromatic compounds. Vogel and Sombröck[23] have prepared the methano[10]annulene 25 with an 81% conversion in the last step (eq. 7). The annulene does not exhibit the same thermal stability as benzocyclopropene or 1H-cyclopropa[b]naphthalene, and polymerizes at room temperature.

\[ \text{Diagram} \]

Cycloproparenes containing considerably more strain than 1 and 2 have also been synthesized. The tetra-dehydrobromination of 26 effected the transformation to the biscyclopropa[b,g]naphthalene 3 (eq. 8) [3]. The high strain energy of this compound is manifested in an explosive decomposition when melted. The less strained homolog 27 has also been prepared (eq. 9) [24].

\[ \text{Diagram} \]
Attempts to prepare 1H-cyclopropa[a]naphthalene via the geminal-dichloride elimination route have failed (eq. 10)[25]. The failure of 28 to give 14 has been rationalized by the tetr subs tituted double bond in 28. The reaction would involve either double bond isomerizations to less substituted (and hence less favorable) positions or the formation of high-energy cyclopropenyl anion intermediates [26]. Thus, the method appears applicable only to linearly fused systems.

Benzocyclopropene has been prepared by the method of Radlick and Crawford (eq. 11) [27] by the lithiation and subsequent internal cyclization of a bromobenzyl methyl ether. Unfortunately, the method fails for the cyclopropa[b]naphthalene[28], and has only been successful in one other case, where 29 was isolated in only 5% yield (eq. 12) [29].
Recently, a new synthetic method has been developed by this laboratory, permitting the synthesis of several previously unknown cycloproparenes. Some of this new work will be presented herein.
THE SYNTHESIS OF
1H-CYCLOPROP[β]PHENANTHRENE

AND

1,2-DIHYDROCYCLOBUT[β]PHENANTHRENE,

AND THE ATTEMPTED

SYNTHESIS OF

1H,5H-BISCYCLOPROP[β,i]ANTHRACENE
BACKGROUND

Although benzocyclopropenes have been known since 1964 [10], the higher homolog anthracene derivatives have appeared only recently, and a stable phenanthrene derivative was unknown. The first cycloprop[b]anthracene derivative was prepared (Scheme III) in 1981 by Müller and Rey[30]. The Diels-Alder reaction of a tetrahalo-cyclopropene and the diene 30, followed by a double-dehydrohalogenation, afforded the gem-dihalocycloprop[b]anthracene 31. This method was successful for the 1,1-dichloro- and 1,1-difluoro- derivatives.

Scheme III

The double-dehydrohalogenation and isomerization of gem-dihalo[4.1.0]heptenes has been used extensively to give the appropriate benzene and naphthalene derivatives.
Unfortunately, the method has met with little success when it was applied to syntheses of the two isomeric compounds 1H-cycloprop[b]anthracene (32) and 1H-cyclopropa[b]phenanthrene (33).

\[
\begin{align*}
&\text{32} & & \text{33} \\
\end{align*}
\]

The reaction of the gem-dichloro-precursor 24 with potassium \text{t}-butoxide readily gives the desired cyclopropa[b]naphthalene (eq. 13), as well as two other products obtained from ring opening. It has been demonstrated that 35 solvolyzes slowly to 34, and that the majority of 34 thus arises from 35 [31].

\[
\begin{align*}
&\text{24} & \rightarrow & \text{2} & + & \text{34} & (\text{eq. 13}) \\
& & & & & \text{35} & \text{X=O-t-Bu} \\
& & & & & & \text{35} & \text{X=Cl} \\
\end{align*}
\]

Similar treatment of the precursor 36 with base, however, did not give the desired cycloprop[b]anthracene. Instead, only 2-(chloromethyl)anthracene and the corresponding \text{t}-butyl ether were obtained (eq. 14) [32].
The prevailing theory at that time for the apparent instability of 32 was a greater degree of bond localization, and also the destabilizing effects of the dimethylenecyclopropane resonance forms of 32 (i.e. 32a, 32b, and 32c).

The apparent instability of 1H-cycloprop[b]anthracene led to interest in its structural isomer, 1H-cyclopropa[b]phenanthrene. The resonance forms available to the phenanthrene derivative include the stable "cyclopropa[b]naphthalene" moiety as well as the various benzene resonances. The difference in resonance energy between anthracene (84 kcal/mol) and phenanthrene (92 kcal/mol) should also help stabilize 33 relative to 32.

Unfortunately, the method was also unsuccessful for
the phenanthrene. The reaction of the appropriate gem-dichloride with potassium t-butoxide gave none of the desired hydrocarbon, and afforded only the ring-opened 2-chloromethyl- and 3-chloromethylphenanthrenes (eq. 15) in the ratio 1:3.5 (by NMR) [33].
The failure of the dehydrohalogenation-isomerization method for the homologs above naphthalene dictated that other approaches be used. The success of the scheme employed by Müller and Rey for 31 indicated that precursors with leaving groups on the bridgehead carbons would be ideal.

Recently the compound 1-bromo-2-chlorocyclopropene 38 has been synthesized by this laboratory[34]. The Diels-Alder reaction of this synthon with the appropriate diene, followed by basic dehydrohalogenation, affords the cyclopropene derivatives unsubstituted at the methylene position (Scheme IV).

Scheme IV

\[
\text{Scheme IV}
\]
The parent compound 1H-cycloprop[b]anthracene has been synthesized in the first use of this synthon. As outlined in Scheme V, the desired diene 30 was reacted with 1-bromo-2-chlorocyclopropene, and the adduct was aromatized with DDQ. The elimination of the halides with potassium t-butoxide afforded 32 in 41.5% yield [35].

Scheme V

![Diagram showing the reaction between 30 and the adduct, resulting in 32 with DDQ and t-BuOK in THF.]

The ease of synthesis of 32 by this method and its apparent stability indicate that failure to form 32 and 33 via elimination and isomerization using the geminal-dichlorides stems from the method itself, and not from any greater degree of bond localization.

The failure of 36 and 37 to yield the desired cyclopropaparenes can be explained via cyclopropylcarbinyl anion intermediates[36]. Base extraction of a proton from
C-2 rather than a bridgehead proton would afford an ary1-stabilized cyclopropylcarbinyl anion (Scheme VI). The increased resonance stabilization of the naphthalene moiety over benzene might account for the failure of the method for 1H-cycloprop[b]anthracene, and its success for 1H-cyclopropa[b]naphthalene.

**Scheme VI**

\[
\begin{align*}
\text{R}= & \text{benzo} \\
\text{Cl} & \\
\end{align*}
\]
RESULTS AND DISCUSSION

The isolation of 1H-cycloprop[b]anthracene as a moderately stable compound rekindled this laboratory's interest in its structural isomer, 1H-cyclopropa[b]phenanthrene. It was first necessary, however, to prepare an appropriate 1,3-diene for the Diels-Alder reaction with 38. The chosen starting material for the synthesis of 33 (via Scheme VII) was dimethyl 3,5,6,7,8,9-hexahydronaphthalene-1,2-dicarboxylate (39), readily available by the Diels-Alder reaction of 1-vinylcyclohexene and dimethyl acetylenedicarboxylate [37].

\[
\begin{array}{c}
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} \\
\end{array}
\]

\[39\]

Reduction of 39 with lithium aluminum hydride in diethyl ether afforded the unsaturated diol 40 in 76% yield. Purification of the diol was accomplished by crystallization from diethyl ether, m.p. 71.5-73.5 °C. Compound 40 was converted to the 1,3-diene 41 using the procedure of Angus and Johnson[38], and was obtained as a colorless oil in 80% yield. An analytical sample of compound 41 was purified by column chromatography on silica gel (hexane); for synthetic purposes the crude material was satisfactory.
Scheme VII

39 \[ \text{CO}_2\text{Me} \] \[ \text{CO}_2\text{Me} \] \[ \text{LiAlH}_4 \] \[ \text{CH}_2\text{OH} \] \[ \text{CH}_2\text{OH} \] \[ \text{TMSI} \] \[ \text{Zn–Cu} \]

38 \[ \text{THF} \] \[ \text{Br} \] \[ \text{Cl} \] \[ \text{DDQ} \]

41 \[ \] \[ 42 \]

43 \[ \text{Br} \] \[ \text{Cl} \] \[ \text{t-BuOK} \]

33
The dihalocyclopropene was prepared via fluoride-induced elimination of TMSCl from 44 in THF (eq. 16). After the preparation of 38, the solution was vacuum distilled into a trap containing the diene, cooled by a liquid nitrogen bath. The reaction mixture was warmed to -20°C and held at this temperature for 6 days.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Br} & \quad \text{TMS} \\
\text{Br} & \quad \text{Cl} \\
\end{align*}
\]  \quad \text{(eq. 16)}

The Diels-Alder adduct 42 was isolated in 57% yield, after purification by column chromatography on silica gel(hexane). The compound was actually a mixture of the regioisomers 42a and 42b, but since the mixture of regioisomers does not affect the subsequent chemistry, it will be ignored for the sake of simplicity in nomenclature and structures.

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Br} \\
\end{align*}
\]  \quad 42a  \quad 42b

Compound 42 could be converted slowly to the aromatized derivative 43 with DDQ in benzene at 50°C-60°C.
for 24 hours. Compound 43 could be isolated in 21% yield after purification by column chromatography on silica gel (hexane) as a colorless oil. The oil slowly crystallized on standing to give a white solid. Treatment of 43 with potassium t-butoxide in THF at -30 °C for 1 hour gave 1H-cyclopropa[b]phenanthrene in 89% yield, purified by column chromatography on Florisil(pentane).

The 1H NMR spectrum of 33 displays the expected pattern with signals at 8 3.59 ppm(s, 2H), 7.70-7.96(m, 6H), 8.52(d, 1H), and 8.70-8.84(m, 1H). The singlet for the bridging methylene group is close to the value reported for the 1H-cycloprop[b]anthracene (3.56 ppm)[33]. The 13C NMR signal for Cl(methylene carbon) appears at 8 19.4 ppm, similar to the value for the anthracene derivative(18.6 ppm). The ultraviolet spectrum(hexane) of 33 exhibits a maximum at 252 nm (ε 56,500) with other absorptions at 320, 327, 335, 343, and 351 nm. The compound exhibits the foul odor common to cycloproparenes, albeit considerably subdued due to the large size of the molecule. The compound is moderately stable at reduced temperatures; a solution of 33 in deuterochloroform showed only slight decomposition after 3 months at -20 °C.

1H-Cyclopropa[b]phenanthrene demonstrates the typical reactivity of cycloproparenes. The reaction of 33 with acetic acid afforded a mixture of the two ring-cleaved products 2- and 3-(acetoxyethyl)phenanthrene(45)(eq. 17,
X=OAc). The observed product ratio was 1:1.5 (by NMR). Similarly, the silver ion-catalyzed reaction of 33 with methanol gave a mixture 2- and 3- (methoxymethyl)-phenanthrene (46) (eq. 17, X=OMe), with an observed product ratio of 1:1 (by NMR).

\[
\begin{align*}
33 & \rightarrow 45 \quad X=OAc \\
& + 46 \quad X=OMe
\end{align*}
\]

(eq. 17)

The less strained higher cycloalkene homologs, the cyclobuta-derivatives, have also been the targets of synthetic chemists. Although several benzocyclobutene derivatives, and even naphthalene and anthracene derivatives are known[39], only one such ring-fused phenanthrene, 1,2-dihydrocyclobuta[1]phenanthrene, has been reported[40]. This compound was synthesized by photolysis of the diene 47 to yield the hydrocarbon 48 (eq. 18). The compound is highly unstable for a benzocyclobutene homolog, and perhaps reflects the typical high reactivity of the localized 9,10-double bond of phenanthrenes.
The availability of the diene 41 from the
cyclopropa[b]phenanthrene synthesis led to interest in the
cyclobuta[b]phenanthrene derivative 49 by this laboratory.

Thummel's method[41] for the generation of benzo-
cyclobutenes from dimethyl cyclobutene-1,2-dicarboxylate
[42] appeared attractive for this synthesis (Scheme VIII).

The diester 50 was prepared via the Diels-Alder
cycloaddition of the 1,3-diene 41 with dimethyl
cyclobutene-1,2-dicarboxylate, accomplished by refluxing in
benzene for 12 hours. The compound was purified by
chromatography on silica gel (hexane:dichloromethane, 2:1)
in 49% yield as a yellow oil, and contained ca. 10% of the
original cyclobutene as an impurity. The ester was
hydrolyzed to the diacid 51 by refluxing with an alcoholic
Scheme VIII

\[
\begin{align*}
41 + 42 & \xrightarrow{\text{KOH}} 50 \\
51 & \xrightarrow{\text{Pb(OAc)}_4} 52 \\
52 & \xrightarrow{\text{DDQ}} 49
\end{align*}
\]
potassium hydroxide solution for 5 hours. The diacid was obtained as a pale yellow solid in 85% yield after recrystallization from dichloromethane. The diacid was converted to the olefinic derivative 52 by stirring with excess lead tetraacetate in dry DMSO for 5 hours at room temperature. Compound 52 was purified by chromatography on silica gel (hexane) and obtained as a white solid in 38% yield. The reaction of 52 with DDQ in benzene effected the conversion to 1,2-dihydrocyclobuta[b]phenanthrene (49) in 49% yield. The compound was purified by chromatography on silica gel (pentane) and obtained as a pale yellow solid.

The $^1$H NMR spectrum of 49 has a similar pattern to that of 33, shifted slightly upfield, with signals at 3.40 ppm (s, 4H) for the methylene protons, and the aromatic signals at 7.50-7.92 (m, 6H), 8.34 (s, 1H), and 8.58-8.67 (m, 1H). The chemical shift of the methylene protons is in good agreement with the value reported for 48 (3.35 ppm) [40].

The extension of the cyclopropaprene series to include 1H-cycloprop[b]anthracene and 1H-cyclopropa[b]phenanthrene led to a desire by this laboratory to approach the bis-annelated anthracene derivative 53.
As with 32 and 33, the most likely approach appeared to be a tetra-dehydrohalogenation on an anthracene skeleton substituted at the bridgehead carbon atoms, as in 54.

![Diagram of structure 54]

The successful use of 1-bromo-2-chlorocyclopropene in the synthesis of other cycloproparenes indicated that a similar Diels-Alder-type reaction sequence should be attempted. Since it was necessary to have a compound substituted at both ends of the molecule, a double-Diels-Alder reaction scheme was envisioned (Scheme IX).

**Scheme IX**

![Diagram of Scheme IX]

\[ X \]
Although the terepane 55 has been reported in the literature [43], it is prepared only with difficulty and in low yields, and suffers from both rapid rearrangement and polymerization. The oxo-bridged terepane 56, however, has been prepared and isolated as a moderately stable compound [44], and has been utilized in Diels-Alder reactions [45] in which cycloaddition was effected on both faces of the terepane. A variety of methods have been reported for removal of the oxygen bridge, with subsequent aromatization of the ring [46].

Scheme X

![Chemical Structures]

53
A collaborative effort was undertaken with P. Vogel, who graciously supplied the starting material for the synthesis of 56. We attempted the synthesis of 53 using the reaction sequence outlined in Scheme X.

Thus, the oxo-tetraene 56 was reacted with 1-bromo-2-chlorocyclopropene using the reaction techniques discussed previously. Examination of the reaction mixture after 6 days indicated that both the starting material 56 and the mono-adduct 57 were present. This mixture was treated with a fresh solution of 38, and the reaction time increased to 17 days, after which time little 38 remained.

The reaction mixture was worked up via the normal procedure, and the residue chromatographed on silica gel (hexane:dichloromethane, 2:1). None of the desired bis-adduct 58 was observed; instead, only the mono-adduct 57 and the tetraene 56 were obtained.

Vogel had noted previously [45] that the addition of the second dienophile to 56 was more difficult, and it was apparent that increased reaction time was not the solution. Therefore, it was decided to explore the use of metal salts to catalyze the addition of the second equivalent of 38 to the mono-adduct 57. Copper(I) and copper(II) salts have been reported as successful catalysts for the Diels-Alder cycloaddition of furans [47], and it was hoped that such salts would also work for our oxygen heterocycle.

Copper(II) acetate was selected, since it is somewhat
soluble in THF, the reaction solvent. Compound 57 and 1-bromo-2-chlorocyclopropene were reacted as before, with the addition of the copper salt, for 6 days (eq. 19). Examination of the reaction mixture after this time showed only starting material, with none of the desired product indicated. The failure of the copper salt led to the investigation of other catalysts.

![Chemical Structure](image)

Lanthanide salts have also been reported as catalysts for the Diels-Alder reaction of oxygen-containing heterocycles [48]. Therefore, the reaction of the tetraene 56 with 38 was conducted with the addition of lanthanum trichloride (eq. 20). Examination of the reaction mixture after 4 days showed primarily tetraene, with some of the mono-adduct present. After 10 days, the percentage of mono-adduct had increased, but there was no indication of the desired bis-adduct.

![Chemical Structure](image)

Continuing in our study of the synthesis of
interestingly aneled cyclopropane, the oxo-bridged mono-adduct 57 was treated with potassium t-butoxide in THF to afford the heterocycle 59 (eq. 21), isolated in 38% yield after chromatography on Florisil (pentane). It is interesting to note that the oxygen bridge distorts the geometry of the molecule sufficiently so that the cyclopropyl protons appear as an AB quartet in the NMR via geminal coupling. Generally, a characteristic singlet is observed for these relatively symmetrical compounds. The cyclopropyl methylene protons appeared at 3.31 ppm.

\[
\begin{align*}
\text{57} & \quad \text{t-BuOK} \quad \rightarrow \quad \text{59} \\
\end{align*}
\]

(eq. 21)

Further work on the synthesis of 1H,5H-biscycloprop[b,i]anthracene is being conducted by this laboratory.
EXPERIMENTAL

General. Proton magnetic resonance spectra were recorded using a Jeol FX90Q (90 MHz) spectrometer. Chemical shifts are reported in δ units (ppm) relative to tetramethylsilane. Unless otherwise noted, NMR spectra were obtained in CDCl₃. Infrared spectra were recorded on a Beckmann 4230 spectrometer as neat films deposited on sodium chloride plates, or as solutions in carbon tetrachloride and carbon disulfide (unless otherwise noted). Ultraviolet spectra were recorded in hexane or pentane solution on a Cary 17 spectrometer. Low-resolution mass spectra were recorded using a Finnigan Model 3300 gas chromatograph/mass spectrometer at 30-40 eV. High resolution mass spectra were recorded using a double-focusing CEC 21-110 mass spectrometer [49].

Solvents and reagents were used as supplied by the manufacturer, or purified by standard methods [50]. Column chromatography was performed on Baker reagent-grade silica gel (60-200 mesh) or Florisil (100-200 mesh). Merck precoated silica gel plates were used for analytical (70 x 25 x 0.25 mm) thin layer chromatography. Reactions requiring inert atmosphere were carried out under prepurified, dry nitrogen.

1,2-bis(hydroxymethyl)-3,5,6,7,8,9-hexahydronaphthalene(40).

Dimethyl 3,5,6,7,8,9-hexahydronaphthalene-1,2-dicarboxylate
39 (10.9 gm, 43.6 mmol) in anhydrous ether (100 ml) was added dropwise over a 30-minute period, to a stirred suspension of 3.31 gm (87.2 mmol) of lithium aluminum hydride in ether cooled to 0°C, under nitrogen atmosphere. The mixture was warmed to room temperature and stirred an additional 4 hours. The flask was again cooled to 0°C and the contents hydrolyzed carefully with 1M aqueous potassium carbonate. The solids were removed by filtration and washed 2X with ether. The combined organics were concentrated, and the residue was crystallized from pentane/dichloromethane to give 5.22 gm of 40, mp. 71.5-73.5°C. Continuous extraction of the solids with refluxing ether for 24 hours afforded 1.28 gm of additional material for a total yield of 6.50 gm (76.8%). NMR 5.36 (brs, 1H), 4.17 (brd, 4H), 2.9-1.0 (m, 13H). IR 3450, 2865, 1590, 1390, 1120, 981 cm⁻¹. Mass spectrum calculated for C₁₂H₁₈O₂: m/e 194.1307; found m/e 194.1303. (Figure 1).

1,2-dimethylene-1,2,3,5,6,7,8,9-octahydonaphthalene (41).
The diol 40 (2.01 gm, 10 mmol) was dissolved in dry ether (40 ml) and dry THF (10 ml) under nitrogen atmosphere. Finely crushed NaI (3.60 gm, 2.4 mmol) was added in one portion, and 6.5 gm of chlorotrimethylsilane was added rapidly dropwise (5 min), and the mixture stirred vigorously for 1 hour.

The Zn-Cu couple was prepared separately, by the method of Angus and Johnson [38]. Dry zinc dust (34 gm, 520 mmol)
and finely crushed CuSO₄·5H₂O (13 gm, 52 mmol) were placed in a 250ml flask fitted with a mechanical stirrer, addition funnel, rubber septum, and nitrogen atmosphere. Dry DMF was added rapidly to the flask, just enough to cover the solids, with vigorous stirring. External cooling was provided with a water bath as necessary. Dry ether(100 ml) was added to the flask after it had cooled to room temperature.

The reaction mixture was transferred via cannula to the Zn-Cu couple over a 45-min. period. The suspension was stirred for 2 hours at room temperature, then the solution was decanted from the solids. The solids were washed 2X with ether, and the combined organic solutions washed 4X with saturated aqueous sodium bicarbonate, and dried over magnesium sulfate. The solvent was removed in vacuo, and the residue chromatographed on silica gel(hexane) to afford 1.28 gm of the 1,3-diene(80%) as a colorless oil. NMR 5.36 (brs, 1H), 5.06 (brd, 2H), 4.76 (m, 2H), 2.9-1.0 (m, 11H). IR 3085, 2936, 2860, 1674, 1630, 1442, 890 cm⁻¹. Mass spectrum calculated for C₁₂H₁₆: m/e 160.1252; found m/e 160.1253. (Figure 2).

1-Bromo-2-chlorocyclopropene (38).

1-Bromo-1-trimethylsilyl-2,2-dichlorocyclopropane 44 (1.31 gm, 5.0 mmol) in dry THF(1.0 ml) was added via syringe to a 1M solution of tetra-n-butylammonium fluoride in THF cooled to -40°C. The mixture was stirred at ca. -20°C for 1 hour.
The flask was cooled to ca. -40°C, and the solvent and volatile products were vacuum distilled (0.005 mm) into a trap containing 5 mmol of the appropriate diene, cooled in a liquid nitrogen bath. It was necessary to warm the reaction flask to room temperature to permit distillation of all of the cyclopropene. The spectral data were in accordance with reported values [34].

1a-Bromo-9a-chloro-1a,2,3,5,6,7,8,8a,9,9a-decahydro-1H-cyclopropa[b]phenanthrene (42).

A solution of the diene 41 (0.64 gm, 4.0 mmol) and 1-bromo-2-chlorocyclopropene (0.767 gm, 5.0 mmol) generated as above was stirred at -20°C for 2 hours, then stored at ca. -20°C for 5 days. TLC (hexane) indicated little diene remained. The solvent was removed in vacuo, the residue taken up in dichloromethane, dried over magnesium sulfate, and the solvent removed in vacuo. The residue was chromatographed on silica gel (hexane) to afford 715 mg of a colorless oil (57%), which crystallized slowly on standing. NMR 5.30 (brs, 1H), 3.6-1.0 (m, 17 H). IR 3070, 3040, 2910, 2840, 2805, 1698, 1440, 1061, 1010, 731 cm⁻¹. Mass spectrum calculated for \( \text{C}_{15}\text{H}_{18}^{79}\text{Br}^{35}\text{Cl} \): m/e 312.0280; found m/e 312.0278. (Figure 3).

1a-Bromo-9a-chloro-1a,2,9,9a-tetrahydro-1H-cyclopropa[b]-phenanthrene (43).
The Diels-Alder adduct 42 (758 mg, 2.42 mmol) was dissolved in dry benzene (25 ml) under nitrogen atmosphere. 3.3 gm (14.5 mmol) of 2,3-dichloro-5,6-dicyanoquinone (DDQ) were added in one portion, and the solution heated at 50-60°C for 24 hours, during which time the insoluble hydroquinone was deposited. The mixture was cooled and the hydroquinone removed by filtration. The solid was washed with hexane/dichloromethane (1:1), and the solvent removed in vacuo. The dark solid was chromatographed on a short silica gel (hexane) column to remove excess DDQ. The solvent was removed in vacuo, and the residue rechromatographed on silica gel (hexane) to give a colorless oil (160 mg, 21.5%) which crystallized slowly on standing. NMR 8.02-7.08 (m, 6H), 4.44-3.36 (m, 4H), 1.56-1.22 (m, 2H). IR 3045, 2920, 2850, 1619, 1596, 1502, 1425, 1069, 1015, 805, 743 cm⁻¹. Mass spectrum calculated for C₁₅H₁₂₂₃Br₅Cl⁻: m/e 305.9810; found m/e 305.9807. (Figure 4).

1H-Cyclopropa[b]phenanthrene (33).

Potassium tert-butoxide (216 mg, 1.93 mmol) was placed in a flask containing dry THF (2.0 ml) under nitrogen atmosphere, and the flask cooled to ca. -50°C. The dihalo derivative 43 (53.1 mg, 0.173 mmol) was dissolved in dry THF (1.5 ml) and added rapidly dropwise to the cooled suspension. The mixture was warmed to ca. -20°C and stirred for 1 hour. The solvent was removed in vacuo, and the residue extracted 4X
with pentane. The washings were centrifuged to remove inorganic salts, and the solvent removed in vacuo. The residue was chromatographed on Florisil (pentane) to afford 33 in 89% yield (29.4 mg). NMR 8.84-8.72 (m, 1H), 8.52 (d, 1H), 7.96-7.54 (m, 6H), 3.59 (s, 2H). 13C NMR 19.43 (C1), 108.37 (C9), 114.28 (C2), 123.01 (C8), 126.31 (C6, C7), 127.67 (C3, C4), 128.50 (C5). UV 250 nm (ε 56,500), 320 nm (748), 327 nm (510), 335 nm (1220), 343 nm (425), 351 nm (1300). IR 3010, 2935, 2390, 1660, 1590, 1500, 1416, 1020 cm⁻¹. Mass spectrum calculated for C₁₅H₁₀: m/e 190.0782; found m/e 190.0781. (Figure 5).

Reaction of 1H-Cyclopropa[b]phenanthrene With Acetic Acid.
Glacial acetic acid (20 microliters) was added to a solution of 33 in deuterochloroform (0.6 ml) in an NMR tube. The tube was allowed to stand at room temperature for 3 days, then the NMR of the ring-opened material was recorded. A mixture of 2-(acetoxyethyl)phenanthrene and the 3-acetoxyethyl derivative (45) was obtained (product ratio 1:1.5 by NMR). No other products were observed, indicating quantitative conversion. NMR 8.82-8.60 (m, 2H), 8.0-7.5 (m, 7H), 5.37, 5.32 (2 singlets, corresponding to the 3- and 2-isomers, respectively, total 2H), 2.16 (s, 3H). Mass spectrum calculated for C₁₇H₁₄O₂: m/e 250.0994; found m/e 250.0990. (Figure 6).

Reaction of 1H-Cyclopropa[b]phenanthrene With Methanol.
The hydrocarbon 33 (11.0 mg, 0.058 mmol), carbon tetrachloride (2 ml), and dry methanol (5 ml) were placed in a flask. One crystal (ca. 1 mg) of silver(I) cyanide was finely crushed, added to the flask, and the mixture stirred at room temperature for 1 hour. The mixture was diluted with dichloromethane (15 ml) and washed with water to remove methanol. The organic phase was dried over magnesium sulfate, and the solvent removed in vacuo to give 10.2 mg (79%) of material, a mixture of 2-(methoxymethyl)phenanthrene and the 3-methoxymethyl isomer (46) (product ratio 1:1 by NMR). NMR 8.77-8.63 (m, 2H), 7.91-7.48 (m, 7H), 4.73, 4.68 (2 singlets, corresponding to the 3- and 2- substituted isomers, total 2H), 3.49, 3.47 (2 singlets, 3H). Mass spectrum calculated for C_{16}H_{14}O: m/e 222.1045; found m/e 222.1040. (Figure 7).

2a, 10a-Dimethyl 1,2,2a,3,4,6,7,8,9,9a,10,10a-dodecahydrocyclobuta[b]phenanthrenedicarboxylate (50).

A solution of the diene 41 (0.80 gm, 5.0 mmol) and dimethylcyclobutene-1,2-dicarboxylate[42] (0.85 gm, 5.0 mmol) in dry benzene(15 ml) was heated to reflux for 12 hours and cooled. TLC (hexane:dichloromethane, 2:1) indicated both starting materials as well as product were present. Further reaction time did not appear to have any effect. The solvent was removed in vacuo, and the residue chromatographed on silica gel (hexane:dichloromethane, 2:1). The diester was isolated
as a yellow oil (810 mg, 49%) with some of the dimethyl
cyclobutene-1,2-dicarboxylate present (90% pure by NMR).
NMR 5.40 (b, s, 1H), 3.77 (s, 6H), 2.9-1.1 (m, 19H). IR
3005, 2940, 2860, 1735, 1435, 1280, 1245, 1116, 1090 cm⁻¹.
Mass spectrum calculated for C₂₀H₂₆O₄: m/e 330.1831; found
m/e 330.1834. (Figure 8).

1,2,2a,3,4,6,7,8,9,9a,10,10a-Dodecahydrocyclobuta[b]-
phenanthrene-2a,10a-dicarboxylic acid (51).
The diester 50 (350 mg, 1.06 mmol), potassium hydroxide (520
mg, 9.29 mmol), water (5 ml), and methanol (12 ml) were placed
in a flask and heated to a gentle reflux for 5 hours. The
solution was cooled and poured into 40 ml of water, then
acidified (to litmus) with concentrated hydrochloric acid.
The aqueous phase was extracted 3X with 40 ml portions of
dichloromethane. The combined organic phases were washed 1X
with water, and dried over magnesium sulfate. The bulk of
the solvent was removed in vacuo, and the acid
recrystallized from dichloromethane as pale yellow crystals
(272 mg, 85%). NMR 7.9 (b, 2H), 5.40 (b, s, 1H), 2.9-1.0
(m, 19H). IR 3700-3100 (acid hydroxyl), 3060, 2920, 2860,
1700, 1435, 1261 cm⁻¹. Mass spectrum calculated for
C₁₈H₂₂O₄: m/e 302.1518; found m/e 302.1517. (Figure 9).

1,2,3,4,6,7,8,9,9a,10-Decahydrocyclobuta[b]phenanthrene(52).
The diacid 51 (222 mg, 0.735 mmol), dry DMSO (15 ml), and
pyridine (130 microliters) were placed in a flask under
nitrogen atmosphere. Lead tetraacetate (600 mg, 1.35 mmol) was added in one portion, and the solution stirred at room temperature for 5 hours. The reaction mixture was poured into 50 ml of water, and extracted 5X with dichloromethane. The combined organic solutions were washed 3X with water, and dried over magnesium sulfate. The solvent was removed in vacuo, and the residue chromatographed on silica gel (hexane). The product was isolated as a white solid (59.5 mg, 38%) containing ca.10% of the 3,10-dehydro derivative as an impurity. NMR 5.35 (brs, 1H), 3.0-1.1 (m, 19H). IR 3010, 2930, 2860, 2840, 1470, 1430, 865, 792 cm⁻¹. Mass spectrum calculated for C₁₆H₂₀: m/e 212.1565; found m/e 212.1564. (Figure 10).

1,2-Dihydrocyclobuta[b]phenanthrene (49).

The hydrocarbon 52 (37.8 mg, 0.178 mmol) and DDQ (183 mg, 0.806 mmol) were dissolved in dry benzene (15 ml) and heated to a gentle reflux for 5 hours. The contents were cooled and 15 ml of hexane/dichloromethane were added. The mixture was filtered to remove excess DDQ and hydroquinone, and the solvent removed in vacuo. The residue was passed through a short silica gel column (hexane) to remove residual DDQ, concentrated, and again chromatographed on silica gel (hexane). The product was isolated as a pale yellow solid (17.9 mg, 49%), mp. 63-65°C. NMR 8.65 (m, 1H), 8.40 (s, 1H), 8.0-7.4 (m, 6H), 3.40 (s, 4H). IR 3045, 2961, 2930,
2855, 1600, 1445, 1255, 900, 870, 800 cm\(^{-1}\). Mass spectrum calculated for \(\text{C}_{16}\text{H}_{12}\): m/e 204.0939; found m/e 204.0934. (Figure 11).

1a-Bromo-7a-chloro-4,5-dimethylene-3,6-oxamethano-1a,2,3-4,5,6,7,7a-octahydro-1H-cyclopropa[b]naphthalene (57).

1,2,4,5-tetramethylene-7-oxanorbornane 56 (752 mg, 5.15 mmol) was reacted with 1-bromo-2-chlorocyclop propane (12 mmol) using the general procedure of 42. After trapping, the reaction mixture was stored at −20 °C for 6 days. Examination of an aliquot revealed that both the tetraene (ca. 70%) and mono-adduct (ca. 30%) were present. The mixture was treated with a fresh solution of 38 and the reaction time increased to 17 days, and the mixture worked up as usual. Chromatography of the residue on silica gel (hexane:dichloromethane, 2:1) gave unreacted tetraene (262 mg) and the mono-adduct 57 (537 mg, 35%) as a pale yellow solid. NMR 5.30 (s, 2H), 5.08 (s, 2H), 4.88 (s, 2H), 3.5-2.6 (m, 4H), 1.7-1.2 (qt, 2H). IR 3080, 2980, 2865, 1725, 1663, 1427, 1062, 902, 838 cm\(^{-1}\). Mass spectrum calculated for \(\text{C}_{13}\text{H}_{12}\text{Br}\text{Cl}\): m/e 297.9760; found m/e 297.9763. (Figure 12).

**Attempted Copper(II) Catalysis of 57.**

The mono-adduct 57 (100 mg, 0.33 mmol) was reacted with 38 using the general procedure of 42 , with the procedure change that 50 mg of copper(II) acetate was added to the
solution as a Diels-Alder reaction catalyst. The mixture was stored at -20°C for 6 days and worked up. The mixture was diluted with dichloromethane (30 ml) and washed exhaustively with water to remove copper acetate and THF. The organics were dried over magnesium sulfate, and the solvent removed in vacuo. None of the desired bis-adduct was observed (by NMR), and only the starting material 57 was recovered.

**Attempted Lanthanide Catalysis of 56.**
The tetraene 56 (382 mg, 2.62 mmol) and 38 were reacted using the general procedure of 42, with the procedure change that ca. 50 mg of lanthanum trichloride was added to the solution as a Diels-Alder reaction catalyst. After 4 days the reaction was checked (by TLC), and showed starting material and the mono-adduct 57, with no indication of the bis-adduct. After 10 days the reaction mixture was worked up. Dichloromethane was added (30 ml) and the organics washed with water to remove the metal salt and THF. The organics were dried, and the solvent removed in vacuo to afford the tetraene 56 (30% by NMR) and the mono-adduct 57 (70%). None of the desired bis-adduct was observed by TLC or NMR.

4,5-Dimethylene-3,6-oxamethano-3,4,5,6-tetrahydro-1H-cyclopropa[b]naphthalene (59).
Potassium tert-butoxide (450 mg, 4.0 mmol) and the dihalo derivative 57 (100 mg, 0.40 mmol) were reacted in THF using the general procedure of 33, for 1 hour. Chromatography on Florisil (pentane) afforded 59 as a white solid (28.4 mg, 39%) with the characteristic foul odor of a benzocyclopropene. NMR 7.18 (s, 2H), 5.56 (s, 2H), 5.30 (s, 2H), 5.18 (s, 2H), 3.4-3.2 (qt, 2H). IR 3085, 3060, 3015, 2940, 2885, 1662, 1365, 880 cm\(^{-1}\). Mass spectrum calculated for \(\text{C}_{13}\text{H}_{10}\text{O}\): m/e 182.0732; found m/e 182.0728. (Figure 13).
THE SYNTHESIS OF
SUBSTITUTED
BENZOCYCLOPROPENES
BACKGROUND

The early interest in possible bond distortions in cyclopropanes led to a desire to prepare compounds incorporating a second small ring fusion on the benzene nucleus. Such bis-annelated compounds have only recently appeared, with the synthesis of 29 and 60 by Garratt and coworkers in 1980 [24, 51].

These compounds were prepared via an elegant synthesis using the elimination/rearrangement method on the appropriate gem-dichloride precursors. Compound 29 was prepared by the sequence outlined in Scheme XI. Although notable as the first good method [29] for the preparation of this strained compound, the procedure is marred by the low yields in the final step. The conversion of 61 to 29 proceeds in 20-40% yield; the higher yields can be obtained only if freshly sublimed potassium tert-butoxide is used.

The preparation of the nonlinear isomer 60 is less straightforward; the analogous route from 62 to 60 failed to give any of the desired product (eq. 22). Relocation of the double bond to the less substituted position as in 63 gave 60 when treated with base. The yields are considerably lower than for 29, on the order of 4-10%
conversion.

Scheme XI

\[
\begin{align*}
\text{RO}_2\text{C} & \xrightarrow{\text{CCl}_2} \text{RO}_2\text{C} & \xrightarrow{\text{LiAlH}_4} \\
\text{RO}_2\text{C} & \xrightarrow{\text{CCl}_2} \text{RO}_2\text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{HOCH}_2 & \xrightarrow{\text{MsCl}} \text{HOCH}_2 & \xrightarrow{\text{t-BuOK}} \\
\text{Cl} & \xrightarrow{\text{MsCl}} \text{Cl} & \xrightarrow{\text{t-BuOK}} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \xrightarrow{\text{hv}} \text{Cl} & \xrightarrow{\text{t-BuOK}} \\
\text{Cl} & \xrightarrow{\text{hv}} \text{Cl} & \xrightarrow{\text{t-BuOK}} \\
\end{align*}
\]

61

29
The failure of the Billups method for 62 has been rationalized in terms of the location of the double bond in the intermediate. Compound 62 contains a very stable tetrasubstituted double bond, and conversion to the cyclopropaprene would involve double bond isomerizations to a less substituted (and less favorable) position. Compound 63 does not require this isomerization.

Two other cyclopropaprenes, containing a simple alkyl substituent, have been prepared by Garratt and coworkers. The 2-methyl- and 3-methylbenzocyclopropaprenes(64 and 65, respectively) have been synthesized via the gem-dichloride route. As in the cases of 29 and 60, multi-step sequences were involved(Scheme XII, Scheme XIII) [52].

Preparation of substituted cyclopropaprenes via the gem-dihalo elimination sequence requires the appropriately substituted dihydrobenzene derivatives for the addition of dichlorocarbene. The tedious syntheses of compounds 29, 60, 64, and 65 reveal that not only are such dihydrobenzenes not readily available, but that they can also be difficult to prepare, and little attention has been directed toward other such compounds.
Scheme XII

Scheme XIII

64

65
RESULTS AND DISCUSSION

The availability of 1-bromo-2-chlorocyclopropene as a cyclopropene synthon led to interest in substituted cyclopropenes by this laboratory. The syntheses of 1H-cycloprop[b]anthracene and 1H-cyclopropa[b]phenanthrene demonstrated the utility of the cycloaddition of 38 with the appropriate 1,3-diene. It was therefore decided that the synthesis of simply-substituted cyclopropenes would be attempted.

Since the linear and nonlinear cyclobuta-derivatives had been prepared, the logical step was preparation of cyclopropenes incorporating the five-membered and six-membered ring fusions (Scheme XIV). An investigation of the literature revealed that all four of the appropriate dienes, i.e. 1,2-dimethylenecyclopentane, 1,2-dimethylene-cyclohexane, 1-vinylcyclopentene, and 1-vinylcyclohexene, were readily available.

Scheme XIV

\[ \text{CH}_2 \quad \text{CH}_2 \quad \text{Br} \quad \text{Cl} \]

\[ \text{CH}_2 \quad \text{CH}_2 \quad \text{Br} \quad \text{Cl} \]

\[ n=2,3,4 \]
1,2-Dimethylenecyclopentane [53] was reacted in a THF solution at \(-20^\circ C\) with 1-bromo-2-chlorocyclopentene \(38\) (generated by the previously described method of fluoride elimination). Workup of the reaction mixture and column chromatography on silica gel (hexane) afforded the Diels-Alder adduct \(66\) in 38\% yield. The treatment of \(66\) with potassium tert-butoxide in THF and chromatography of the reaction mixture gave 3,4,5-trihydro-1H-cycloprop[f]-indene \(67\) in 83\% yield (eq. 23). The bridging methylene signal of the NMR spectrum of \(67\) appeared at 3.35 ppm.

![Chemical structure](image)

\[\text{eq. 23}\]

The reaction of \(38\) with 1,2-dimethylenecyclohexane[53] in THF afforded the Diels-Alder adduct \(68\), isolated in 48\% yield after chromatography on silica gel (hexane). The treatment of \(68\) with base and normal workup gave 3,4,5,6-tetrahydro-1H-cyclopropa[b]naphthalene \(69\) in 96\% yield (eq. 24). The bridging methylene signal appeared at 3.21 ppm.

![Chemical structure](image)

\[\text{eq. 24}\]
The reaction of 38 with 1-vinylcyclopentene[41] in THF afforded the Diels-Alder adduct 70 in 26% yield after purification. This yield is considerably lower than the yields of the "locked" dimethylene compounds, and reflects the greater degree of rotational freedom of the acyclic vinyl group. Treatment of 70 with base and normal workup gave 4,5,6-trihydro-1H-cycloprop[e]indene 71 in 44% yield (eq. 25). The bridging methylene signal appeared at 3.20 ppm.

\[
\begin{align*}
\text{38} & \rightarrow \text{70} & \rightarrow \text{71} \\
\end{align*}
\]

(eq. 25)

The reaction of 38 with 1-vinylcyclohexene[54] in THF afforded the Diels-Alder adduct 72 in 36% yield after purification. Treatment with base and normal workup gave 4,5,6,7-tetrahydro-1H-cycloprop[a]naphthalene 73 in 80% yield (eq. 26). The bridging methylene signal appeared at 3.15 ppm.

\[
\begin{align*}
\text{38} & \rightarrow \text{72} & \rightarrow \text{73} \\
\end{align*}
\]

(eq. 26)
The ease of synthesis of these new aneled compounds via the two-step cycloaddition/elimination sequence indicated that it might be a more convenient route to the previously known substituted cyclopropanes. Hence, four other dienes were employed: 1,2-dimethylenecyclobutane; 1-vinylcyclobutene; 1-methyl-1,3-butadiene; and 2-methyl-1,3-butadiene.

The reaction of 38 with 1,2-dimethylenecyclobutane[53] in THF afforded the Diels-Alder adduct 74 in 19% yield, as well as another product of the same mass presumed to be the 1,2 adduct. Although the structure of the second adduct has not been confirmed, the dimethylenecyclobutane has a known propensity for 1,2- rather than 1,4- addition[57]. Although separation of these compounds was difficult, it could be accomplished by repeated chromatography on silica gel (hexane). Treatment of 74 with base and normal workup gave 29 in 46% yield (eq. 27).

![Chemical reaction](image)

The reaction of 38 with 1-vinylcyclobutene[41] in THF afforded the Diels-Alder adduct 75 in 21% yield after purification. Treatment with base and normal workup gave 60 in 45% yield (eq. 28).
The reaction of 38 with 1-methyl-1,3-butadiene in THF afforded the Diels-Alder adduct 76 in 13% yield after purification. As with the vinylcycloalkenes, the yields are considerably reduced due to the greater conformational freedom of the acyclic diene. Treatment with base and normal workup gave 64 in 36% yield (eq. 29).

The reaction of 38 with 2-methyl-1,3-butadiene in THF afforded the Diels-Alder adduct 77 in 12% yield after purification. Treatment of 77 with base and normal workup gave 65 in 32% yield (eq. 30).

From our results in this series of annelated
cyclopropenes 67, 69, 71, and 73, and the previously known compounds, it can be seen that the method is readily adaptable, with the selection of the appropriate diene, to a wide variety of cyclopropenes. Thus, Vogel's biscyclopropanaphthalene 3 was prepared in this laboratory via the cycloaddition of the diene 78 (known from Garratt's synthesis of 29) [51] with 1-bromo-2-chlorocyclopropene, followed by treatment of the tetrahalo derivative 79 with base (eq. 31).

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{78} & \quad \text{79} \\
\end{align*}
\]

(eq. 31)

The Diels-Alder adduct 79 was obtained in 42% yield as a white solid, after recrystallization from hexane. Since compound 79 contained the geminal-dichloride moiety, the reaction time and temperature were adjusted accordingly. A solution of 79 in dry THF was added to a suspension of potassium tert-butoxide in THF at ca. -40°C. The mixture was warmed to room temperature and stirred for ca. 4 hours, then worked up via the usual procedure. Chromatography on Florisil(pentane) gave 3 as a white solid in 52% yield.

The newly synthesized compounds 67, 69, 71, and 73
exhibited the expected physical properties of benzocyclopropenes. For the linear isomers 67 and 69, the NMR signals of both the aromatic and bridging methylene protons appeared as singlets, in accordance with cyclopropa[4.5]benzocyclobutene. For the nonlinear isomers 71 and 73, however, the aromatic signals appeared as an AB quartet from ortho coupling, also in accordance with the nonlinear cyclopropa[3.4]benzocyclobutene. The $^1$H NMR data of some benzocycloalkenes are presented in Table III.

The ultraviolet spectra of the annelated benzocyclopropenes exhibit an interesting pattern (Table IV). For the meta-fused isomers, ring strain has little effect, and the spectra correspond well to the 1,2,3,4-tetraalkylbenzenes, with a bathochromic shift occurring with larger alkyl substituent size. The para-fused isomers, however, exhibit a shift to longer wavelength with reduction in alkyl ring size (increased strain). These data support Thummel's contention that it is not the amount of strain, but the position at which that strain is introduced, which is critical in perturbing the electronic spectrum[41]. Such behavior of bis-annelated benzenes has been rationalized [57] from the hyperconjugative abilities of the fused rings, and changes in the configurational composition of the lowest excited singlet state.
<table>
<thead>
<tr>
<th>Ar-H</th>
<th>Structure 1</th>
<th>Structure 2</th>
<th>Structure 3</th>
<th>Structure 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.19-7.15</td>
<td>3.11</td>
<td>7.08-6.80</td>
<td>3.06</td>
<td>2.34 (methyl)</td>
</tr>
<tr>
<td>7.04-6.82</td>
<td>3.18</td>
<td>3.24</td>
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<tr>
<td>6.85</td>
<td>3.08</td>
<td>3.08</td>
<td>7.15</td>
<td>3.35</td>
</tr>
<tr>
<td>6.88</td>
<td>3.14</td>
<td>7.07-6.80</td>
<td>3.12</td>
<td>2.85-2.77</td>
</tr>
<tr>
<td>6.91</td>
<td>3.08</td>
<td>2.86</td>
<td>2.00</td>
<td></td>
</tr>
</tbody>
</table>
Table IV
Ultraviolet Data of Benzocycloalkenes

|  | \( \lambda_{\text{max}} \) nm |
|---|---|---|---|---|---|---|
| ![Structure 1](structure1.png) | 276 | 263 | 255 | ![Structure 2](structure2.png) | 277 | 270 | 264 |
| ![Structure 3](structure3.png) | 284 | 277 | 270 | ![Structure 4](structure4.png) | 271 | 265 | 259 |
| ![Structure 5](structure5.png) | 276.5 | 270 | 264 | ![Structure 6](structure6.png) | 294 | 287.5 | 284 |
| ![Structure 7](structure7.png) | 280 | 272 | 266 | ![Structure 8](structure8.png) | 292 | 283 | 274 |
| ![Structure 9](structure9.png) | 283 | 275 | 267 | ![Structure 10](structure10.png) | 289 | 282 | 274 |
| ![Structure 11](structure11.png) | 275 | 269 | 266 | ![Structure 12](structure12.png) | 286 | 280 | 276 |
| ![Structure 13](structure13.png) | 276 | 271 | 267 | ![Structure 14](structure14.png) | 286 | 280 | 276 |
Cycloproparenes are known to react with a variety of reagents. The reactions of these compounds with electrophiles are particularly interesting, and have been explored in some detail for the simple substituted cycloproparenes known previously. The reactions of the newly synthesized cycloproparenes presented here will be reported in the next section.
EXPERIMENTAL

General. Please see the Experimental section for 1H-cyclopropa[b]phenanthrene.

1a-Bromo-6a-chloro-1a,2,3,4,5,6,6a-heptahydro-1H-cyclopropa-[f]indene (66).
1,2-Dimethylenecyclopentane [53] (0.50 gm, 5.3 mmol) was reacted with 1-bromo-2-chlorocyclopentene (0.767 gm, 5.0 mmol) as described previously for 33. After trapping, the reaction mixture was stored at -20°C for 2 days. The solvent was removed in vacuo, the residue taken up in dichloromethane, dried over magnesium sulfate, and the solvent removed in vacuo. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (472 mg, 38%). NMR 3.1-2.7 (brd, 4H), 2.5-2.0 (m, 4H), 1.9-1.5 (m, 2H), 1.44 (d, 2H). IR 2960, 2900, 2850, 1440, 1072 cm\(^{-1}\). Mass spectrum calculated for \(\text{C}_{10}\text{H}_{12}\text{Br}^{35}\text{Cl}\): m/e 245.9811; found m/e 245.9816. (Figure 14).

1a-Bromo-7a-chloro-1a,2,3,4,5,6,7,7a-octahydro-1H-cyclopropa[b]naphthalene (68).
1,2-Dimethylenecyclohexane [53] (0.70 gm, 6.5 mmol) was reacted with 1-bromo-2-chlorocyclohexene (5.0 mmol) using the general procedure of 66, for 5 days. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (634 mg, 48%). NMR 3.1-2.4 (m,
4H), 2.0-1.1 (m, 10H). IR 2930, 2820, 1435, 1060, 1010 cm⁻¹. Mass spectrum calculated for C_{11}H_{14}^{79}Br^{35}Cl: m/e 259.9967; found m/e 259.9970. (Figure 15).

**1a-Bromo-6b-chloro-1a,2,4,5,6,6a,6b-heptahydro-1H-cyclopropa[е]indene (70).**

1-Vinylcyclopentene [41] (0.85 gm, 9.0 mmol) was reacted with 1-bromo-2-chlorocyclopropene (5.0 mmol) using the general procedure of 66, for 3 days. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (324 mg, 26%). NMR 5.25 (m, 1H), 3.2-2.7 (m, 3H), 2.6-1.4 (m, 6H), 1.25 (m, 2H). IR 3090, 3020, 2960, 2870, 1670, 1630, 1410, 1105 cm⁻¹. Mass spectrum calculated for C_{12}H_{13}^{79}Br^{35}Cl: m/e 245.9811; found m/e 245.9816. (Figure 16).

**1a-Bromo-7b-chloro-1a,2,4,5,6,7,7a,7b-octahydro-1H-cyclopropa[b]naphthalene (72).**

1-Vinylcyclohexene [54] (0.50 gm, 4.63 mmol) was reacted with 1-bromo-2-chlorocyclopropene (5.0 mmol) using the general procedure of 66, for 40 hours. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (432 mg, 36%). NMR 5.1 (m, 1H), 3.5-1.1 (m, 13H). IR 3040, 2935, 2850, 1700, 1665, 1445, 1260, 730 cm⁻¹. Mass spectrum calculated for C_{11}H_{14}^{79}Br^{35}Cl: m/e 259.9967; found m/e 259.9970. (Figure 17).
3,4,5-Trihydro-1H-cyclopropa[f]indene (67).

Potassium tert-butoxide (500 mg, 4.46 mmol) was placed in a flask containing dry THF (2.0 ml) under nitrogen atmosphere. The flask was cooled to ca. -50°C. The dihalo derivative 66 (124 mg, 0.503 mmol), was taken up in dry THF (1.0 ml) and added rapidly to the cooled suspension. The mixture was warmed to ca. -20°C and stirred for 1 hour. The bulk of the solvent was removed in vacuo, and the residue washed 4X with pentane. The washings were centrifuged to remove inorganic salts, and the solvent removed in vacuo. The residue was chromatographed on Florisil (pentane) to give nearly pure 67 (54.4 mg, 83%) as a pale yellow oil. NMR 7.15 (s, 2H), 3.35 (s, 2H), 3.05-2.85 (t, 4H), 2.28-1.92 (m, 2H). UV 274 nm (ε 1522), 283 nm (21°), 292 nm (1689). IR 3045, 2940, 2840, 1655, 1450, 1345, 1055, 835 cm⁻¹. Mass spectrum calculated for C₁₀H₁₀: m/e 130.0783; found m/e 130.0785. (Figure 18).

3,4,5,6-Tetrahydro-1H-cyclopropa[b]naphthalene (69).

Potassium tert-butoxide (500 mg, 4.46 mmol) and the dihalo derivative 68 (153 mg, 0.589 mmol) were reacted using the general procedure used for 67. Chromatography on Florisil (pentane) afforded 69 as a yellow oil (81.7 mg, 96%). NMR 6.97 (s, 2H), 3.21 (s, 2H), 2.90-2.65 (m, 4H), 1.90-1.65 (m, 4H). UV 274 nm (ε 9210), 282 nm (12600), 289 nm (10700). IR 3050, 3020, 2940, 2860, 1670, 1455, 1355, 1055, 840 cm⁻¹. Mass spectrum calculated for C₁₁H₁₂: m/e 144.0939; found
m/e 144.0938. (Figure 19).

4,5,6-Trihydro-1H-cycloprop[a]indene (71).
Potassium tert-butoxide (500 mg, 4.46 mmol) and the dihalo derivative 70 (150 mg, 0.606 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 71 as a colorless oil (34.9 mg, 44%). NMR 7.20-7.00 (qt, 2H), 3.20 (s, 2H); 3.05-2.80 (m, 4H), 2.3-1.9 (m, 2H). UV 266 nm ( ε 929), 272 nm (1212), 280 nm (1214). IR 3050, 2945, 2845, 1670, 1455, 1050, 795 cm⁻¹. Mass spectrum calculated for C_{10}H_{10}: m/e 130.0783; found m/e 130.0785. (Figure 20).

4,5,6,7-Tetrahydro-1H-cycloprop[a]naphthalene (73).
Potassium tert-butoxide (1.2 gm, 10.7 mmol) and the dihalo derivative 72 (112 mg, 0.43 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 73 as a colorless oil (49.7 mg, 80%). NMR 7.13-6.90 (m, 2H), 3.15 (s, 2H), 2.80 (brd, 4H), 1.85 (m, 4H). UV 267 nm ( ε 462), 275 nm (695), 283 nm (672). IR 3045, 2920, 2845, 1675, 1460, 1255, 1060, 800 cm⁻¹. Mass spectrum calculated for C_{11}H_{12}: m/e 144.0939; found 144.0938. (Figure 21).

5-Bromo-4-chloro-3,4,5,6-tetrahydro-7H-cyclopropa[4.5]benzo-cyclobutene (74).
1,2-Dimethylenecyclobutane [53] (0.50 gm, 6.2 mmol) was
reacted with 1-bromo-2-chlorocyclopropene (5 mmol) using the general procedure of 66, for 6 days. The Diels-Alder adduct (222 mg, 19%) and a second product of the same mass, presumed to be the 1,2-adduct (438 mg), were obtained. Separation of these isomers was difficult, and was accomplished by repeated chromatography on silica gel (hexane). NMR 3.0-2.7 (m, 4H), 2.5-2.0 (m, 4H), 1.5 (d, 2H). IR 2980, 2940, 2900, 2840, 1430, 1410, 1060 cm⁻¹. Mass spectrum calculated for C₉H₇OBr₃Cl: m/e 231.9654; found m/e 231.9650. (Figure 22).

4-Bromo-3-chloro-2,3,4,5-tetrahydro-7H-cyclopropa[3.4]benzocyclobutene (75).

1-Vinylcyclobutene[41] (0.57 gm, 7.1 mmol) was reacted with 1-bromo-2-chlorocyclopropene (5 mmol) using the general procedure of 66, for 5 days. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (250 mg, 21%). NMR 5.25-5.00 (m, 1H), 3.50 (m, 1H), 3.0-1.5 (m, 6H), 1.3-1.1 (m, 2H). IR 3050, 2995, 2925, 2825, 1685, 1410, 1210, 1090, 830 cm⁻¹. Mass spectrum calculated for C₉H₇OBr₃Cl: m/e 231.9654; found m/e 231.9650. (Figure 23).

6-Bromo-1-chloro-2-methylbicyclo[4.1.0]hept-3-ene (76).

1-methyl-1,3-butadiene [58] (0.95 gm, 14 mmol) was reacted with 1-bromo-2-chlorocyclopropene (5 mmol) using the general
procedure of 66, for 5 days. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (146 mg, 13%). NMR 5.7-5.1 (m, 2H), 3.2-2.7 (m, 3H), 1.7-1.1 (m, 5H). IR 3040, 2975, 2935, 2880, 1662, 1455, 1200, 1040 cm⁻¹. Mass spectrum calculated for \( \text{C}_8\text{H}_{10}^7\text{Br}^{35}\text{Cl} \): m/e 219.9654; found m/e 219.9656. (Figure 24).

6-Bromo-1-chloro-3-methylbicyclo[4.1.0]hept-3-ene (77).
2-methyl-1,3-butadiene [58] (0.95 gm, 14 mmol) was reacted with 1-bromo-2-chlorocyclopropene (5 mmol) using the general procedure of 66, for 5 days. The Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a colorless oil (136 mg, 12%). NMR 5.3-5.0 (m, 1H), 3.0-2.6 (m, 4H), 1.8-1.2 (m, 5H). IR 3050, 2970, 2909, 2841, 1640, 1440, 1080 cm⁻¹. Mass spectrum calculated for \( \text{C}_8\text{H}_{10}^7\text{Br}^{35}\text{Cl} \): m/e 219.9654; found m/e 219.9656. (Figure 25).

Potassium tert-butoxide (140 mg, 1.25 mmol) and the dihalo derivative 74 (51.6 mg, 0.22 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 29 as a yellow oil (11.8 mg, 46%). The spectral data were in accordance with reported values [51].

7H-Cyclopropa[3.4]benzocyclobutene (60).
Potassium tert-butoxide (570 mg, 5.08 mmol) and the dihalo derivative 75 (100 mg, 0.43 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 66 as a yellow oil (22.2 mg, 45%). The spectral data were in accordance with reported values [51].

2-Methylbenzocyclopropene (64).
Potassium tert-butoxide (150 mg, 1.34 mmol) and the dihalo derivative 76 (76.1 mg, 0.34 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 64 as a pale yellow oil (12.8 mg, 36%). The spectral data were in accordance with reported values [52].

3-Methylbenzocyclopropene (65).
Potassium tert-butoxide (150 mg, 1.34 mmol) and the dihalo derivative 77 (77.4 mg, 0.35 mmol) were reacted using the general procedure of 67. Chromatography on Florisil (pentane) afforded 65 as a colorless oil (11.5 mg, 32%). The spectral data were in accordance with reported values [52].

3a-Bromo-1,1,4a-trichloro-1a,2,3,3a,4a,5,6,6a-octahydro-1H,-4H-biscyclopropa[b.g]naphthalene (79).
7,7-Dichloro-1,2-dimethylenebicyclo[4.1.0]heptane [51] (945 mg, 5 mmol) and 1-bromo-2-chlorocyclopropene (5 mmol) were reacted using the general procedure of 66, for 6 days. The
Diels-Alder adduct was chromatographed on silica gel (hexane) and isolated as a white solid recrystallized from hexane in 42% yield. NMR 2.90-2.60 (m, 4H), 2.30-2.00 (brs, 4H), 1.90-1.70 (t, 2H), 1.52-1.29 (qt, 2H). IR 2890, 2825, 1420, 1325, 1050, 1000, 895 cm⁻¹. Mass spectrum calculated for C₁₂H₁₂Br₃₅Cl₃: m/e 339.9188; found m/e 339.9187. (Figure 26).

1H,4H-Biscyclopropabq)naphthalene (3).

Potassium tert-butoxide (500 mg, 4.46 mmol) was placed in a flask sealed with a rubber septum, under nitrogen atmosphere. Dry THF (2.0 ml) was added, and the flask cooled to ca. -40°C. The tetrahalo derivative 79 (52.5 mg, 0.15 mmol) in THF (1.0 ml) was added rapidly dropwise to the cooled suspension. The mixture was stirred at ca. -20°C for 30 minutes, warmed to room temperature, and stirred for 4 hours. The solvent was removed in vacuo and the residue washed 4X with pentane. The pentane washings were centrifuged to remove inorganic salts, and the solvent removed in vacuo. The residue was chromatographed on Florisil (pentane) to afford 3 as a white solid in 52% yield. The spectral data were in accordance with reported values [3].
THE REGIOSELECTIVE
REACTIIONS OF
ANNELATED
BENZOCYCLOPROPENES
BACKGROUND

Cyclopropenes react with a variety of reagents, and cleavage of the three-membered ring is predominate, reflecting the strained character of the bicyclic ring fusion. Ring cleavage is readily accomplished with mineral acids, halogens, and silver(I) ion catalysis.

The Ag(I)-catalyzed reaction of benzocyclopropene with alcohols, thiols, and amines all occur readily at 0°C in aprotic solvents to give the corresponding benzylated derivatives in high yields (eq. 32) [59]. The reaction is considerably slower without the silver ion; methanolysis of benzocyclopropene gave less than 8% of the ether after 24 hours.

\[
\begin{align*}
\text{Cyclopropene} & \xrightarrow{\text{Ag}^+} \text{Benzocyclopropene} & \rightarrow \text{Benzylated derivative} \\
\text{eq. 32}
\end{align*}
\]

Mineral acids react readily with cyclopropenes to give the arylmethyl derivatives, and this reaction has been used for the characterization of some cyclopropenes [60]. Reaction of 3-chlorobenzocyclopropene with hydrochloric acid yielded a mixture of 3- and 4-chlorobenzyl chloride (eq. 33) [61]. Reaction of 22 with Ag(I) and alcohol, however, gave only the 4-chlorobenzyl ether (eq. 34) [21].
In contrast to the mixture obtained from 22, reaction of the nonlinearly fused 60 with hydrochloric acid gave only one product, which seemed to indicate the substitution pattern in unsymmetrical systems could influence the direction of cleavage (eq. 35) [51].

In an effort to test the concept of controlled directional cleavage of the three-membered ring, Garratt and coworkers reacted the three asymmetrically substituted cyclopropabenes 64, 65, and 60 with several reagents[52].

Compound 64, when reacted with iodine, bromine,
hydrochloric acid, Ag(I)-ethanol, and Ag(I)-aniline, gave only a mixture of the products of type 80 and 81 (eq. 36). Similarly, compound 65 gave only a mixture of 82 and 83 (eq. 37). Although some selectivity was apparent, it was not generally enough to be synthetically useful.

\[
\begin{align*}
\text{CH}_3 & \quad \text{XY} & \quad \text{CH}_3 \\
64 & \quad \text{CH}_2Y & \quad X \\
& \quad \text{CH}_2Y & \quad \text{CH}_3 \\
& \quad \text{X} & \quad \text{XY} \\
65 & \quad \text{H}_3C & \quad \text{XY} \\
\end{align*}
\]

(eq. 36)

\[
\begin{align*}
\text{H}_3C & \quad \text{XY} & \quad \text{CH}_2Y & \quad \text{H}_3C \\
65 & \quad \text{XY} & \quad \text{CH}_2Y & \quad \text{H}_3C \\
& \quad \text{X} & \quad \text{X} & \quad \text{X} \\
& \quad \text{X} & \quad \text{X} & \quad \text{X} \\
82 & \quad \text{X} & \quad \text{X} & \quad \text{X} \\
83 & \quad \text{X} & \quad \text{X} & \quad \text{X} \\
\end{align*}
\]

(eq. 37)

\(X=\text{Y}=\text{Br}; \quad X=\text{Y}=\text{I}; \quad X=\text{H},\text{Y}=\text{Cl}; \quad X=\text{H},\text{Y}=\text{OE}\text{t}; \quad X=\text{H},\text{Y}=\text{NHPh}\)

The reaction of 60 with electrophiles, however, did not produce the mixtures observed for 64 and 65. Instead, it was found that iodine gave predominately, and bromine exclusively, products of type 84 (eq. 38) \((X=\text{Y}=\text{Br or I})\).

\[
\begin{align*}
& \quad \text{XY} \\
60 & \quad \text{XY} \\
& \quad \text{CH}_2Y \\
& \quad \text{X} \\
& \quad \text{CH}_2Y \\
& \quad \text{X} \\
& \quad \text{X} \\
84 & \quad \text{X} \\
85 & \quad \text{X} \\
\end{align*}
\]

(eq. 38)

The addition of HCl and Ag(I)-ethanol to 60 gave
exclusively products of type 85 (eq. 38) (X=H, Y=Cl, or OEt).

The increased regioselectivity of 60 to electrophilic substitution by halogens has been justified by the electrophilic substitution pattern of benzocyclobutene[62]. Substitution in benzocyclobutene occurs at the beta-aryl carbon, due to the greater charge stabilization of the alpha-cation 86 over the aryl-beta cation 87. The stabilization has been attributed to the rehybridization of the sigma-bond framework due to the bond angle requirements of the fused four-membered ring. The aryl carbon bonding to the four-membered ring has greater p-character in the small ring bond, and hence greater s-character in the bond to the alpha carbon. The s-orbital is capable of greater charge dispersion, and is better able to stabilize a positive charge.

![Diagram showing structures 86, 87, and 88](image)

Similar electrophilic attack in 60 would give an intermediate with the positive charge at the aryl-alpha carbon, as in 88. This intermediate could then cleave to the benzylic cation, giving the observed product.
The reaction of 60 with silver ion and with acids is thought to proceed through the cleavage of the cyclopropyl sigma bond, opening to a benzylic cation with an initial partial charge distribution as illustrated in 89.

As with the electrophilic addition of halogen, this orientation places any positive charge at the preferred aryl-alpha carbon. The reaction of acid with the cyclopropyl sigma electrons, rather than the pi system via electrophilic attack has been attributed to the increased strain (and hence increased reactivity) of the sigma framework due to the fusion of the second strained ring. The conclusion that the strain is concentrated in the sigma framework rather than the pi-electrons has been based on the normality of the electronic spectrum.
RESULTS AND DISCUSSION

The availability of the four cycloproparenes incorporating the additional five- and six-membered ring fusions (67, 69, 71, and 73) in this laboratory led to the desire to conduct further product studies in the cycloproparene series. Electrophiles similar to those used by Garratt were chosen; i.e. bromine, iodine, acetic acid, hydrochloric acid, and silver ion/methanol.

The reaction of the linearly fused isomers 67 and 69 under conditions identical to those used for the nonlinearly fused compounds was conducted, since these compounds could give only one ring-opened product. Regardless of the reagent, the beta-aryl derivative would be obtained, providing "authentic" samples for direct comparison with the products derived from 71 and 73.

The linearly fused indene 67 was treated with bromine in carbon tetrachloride at reduced temperature (eq. 39, X=Br). Removal of the solvent in vacuo cleanly afforded the ring-cleaved product 90 as a yellow oil in 82% yield. The bromomethyl protons appeared in the NMR as a singlet at 4.60 ppm, and the aromatic signals appeared as two singlets at 7.42 and 7.30 ppm. Compound 67 was treated similarly.
with iodine (eq. 39, X=I) to give 91 as a yellow oil (72%), in which the iodomethyl signal appeared at 4.56 ppm.

\[
\text{67} \xrightarrow{\mathrm{X}_2} \text{90} \quad \text{X=Br} \\
\text{91} \quad \text{X=I}
\]

(eq. 39)

Compound 67 was treated with hydrochloric acid in carbon tetrachloride solution to afford the chloromethyl derivative 92 (eq. 40, X=Cl) as a colorless oil in 72% yield. The chloromethyl protons appeared in the NMR as a singlet at 4.58 ppm. The reaction of 67 with acetic acid yielded the acetate 93 (76%) (eq. 40, X=OAc). The acetoxyethyl protons appeared at 5.05 ppm. The silver-catalyzed reaction of 67 with methanol gave the benzyl ether 94 as a colorless oil in 70% yield (eq. 40, X=OMe), in which the methoxymethyl protons appeared at 4.43 ppm.

\[
\text{67} \xrightarrow{\mathrm{HX}} \text{92} \quad \text{X=Cl} \\
\text{93} \quad \text{X=OAc} \\
\text{94} \quad \text{X=OMe}
\]

(eq. 40)

The linearly fused 69 was treated similarly. Reaction of 69 with bromine gave the ring-cleaved dibromide 95 as a yellow oil in 85% yield (eq. 41). The bromomethyl protons
appeared at 4.56 ppm.

\[ \text{69} \xrightarrow{\text{Br}_2} \text{95} \]  
(eq. 41)

The reaction of 69 with hydrochloric acid afforded the chloromethyl derivative 96 (eq. 42, X=Cl) as a colorless oil in 74% yield. The chloromethyl protons appeared in the NMR as a singlet at 4.52 ppm. The reaction of 69 with acetic acid yielded the acetate 97 (69%) (eq. 42, X=OAc). The acetoxyethyl protons appeared at 5.03 ppm. The silver-catalyzed reaction of 69 with methanol gave the benzyl ether 98 as a colorless oil in 77% yield (eq. 42, X=OMe), in which the methoxymethyl protons appeared at 4.39 ppm.

\[ \text{69} \xrightarrow{\text{HX}} \text{96 X}=\text{Cl} \]  
97 X=OAc  
98 X=OMe

The nonlinearly fused indene 71 was treated with bromine to give the aryl-alpha ring opened product 99 exclusively, in 78% yield (eq. 43, X=Br). The bromomethyl protons appeared at 4.64 ppm, and the aromatic signals appeared as a symmetrical multiplet (7 peaks) at 7.4-6.9 ppm. Compound 71 was treated similarly with iodine, but a
mixture of the ring-cleaved products \( 100 \) and \( 101 \) was obtained (eq. 43, \( X=I \)). The product ratios were determined (by NMR) as 68:32 with respective methylene shifts of 4.60 and 4.51 ppm, in a combined yield of 74%. Similar results were obtained by Garratt with \( 60 \); reaction with bromine gave exclusively one product, while iodine gave a mixture.

\[ \begin{array}{c}
\text{71} \\
X_2 \\
\rightarrow \\
\text{CH}_2X \\
\text{X} \\
+ \\
\text{X} \\
\text{CH}_2X \\
\text{(eq. 43)}
\end{array} \]

The reaction of 71 with hydrochloric acid afforded the chloromethyl derivative \( 102 \) (eq. 44, \( X=Cl \)) as a colorless oil in 68% yield. The chloromethyl protons appeared in the NMR as a singlet at 4.58 ppm. The reaction of 71 with acetic acid gave the acetate \( 103 \) in 71% yield (eq. 44, \( X=OAc \)), in which the acetoxyethylene protons appeared at 5.05 ppm. The silver-catalyzed reaction of 71 with methanol gave the benzyl ether \( 104 \) as a colorless oil.

\[ \begin{array}{c}
\text{71} \\
\text{HX} \\
\rightarrow \\
\text{CH}_2X \\
\text{H} \\
\text{(eq. 44)}
\end{array} \]

\( 102 \) \( X=Cl \)  
\( 103 \) \( X=OAc \)  
\( 104 \) \( X=OMe \)
in 75% yield (eq. 44, X=OMe). The methoxymethyl protons appeared at 4.43 ppm.

The nonlinearly fused compound 73 was treated with bromine, but in this case a mixture of both ring-opened products 105 and 106 was obtained (eq. 45), with a product distribution of 80:20 (by NMR). The bromomethyl protons of 105 appeared at 4.68 ppm, and 106 appeared at 4.65 ppm. The combined yield of 105 and 106 was 80%.

![Chemical structure diagram]

The reaction of 73 with hydrochloric acid afforded a mixture of the chloromethyl derivatives 107 and 108 (eq. 46, X=Cl) in a total yield of 72%. The product ratio was 45:55 by NMR, with methylene singlets at 4.59 and 4.52 ppm, respectively. The reaction of 73 with acetic acid gave a mixture of the acetates 109 and 110 (product ratio 33:67 by NMR) in 66% yield, with methylene signals at 5.08 and 5.03 ppm (eq. 46, X=OAc). The silver-catalyzed reaction of 73 with methanol afforded a mixture of the benzyl ethers 111 and 112 (product ratio 44:56 by NMR) in 72% overall yield (eq. 46, X=OMe). The methylene signals of the ethers appeared at 4.43 and 4.39 ppm, respectively.
The overall pattern is clear: the cycloproparene $\text{71}$, incorporating the meta-fused five-membered ring, cleaves regioselectively to give predominately one product. The cycloproparene $\text{73}$, which incorporates the meta-fused six-membered ring, cleaves the three-membered ring in both directions to give a mixture of products. The product distributions are presented in Table V.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>% alpha</th>
<th>% beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{71}$</td>
<td>Bromine</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Iodine</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>HOAc</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Ag+/MeOH</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>$\text{73}$</td>
<td>Bromine</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>HOAc</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Ag+/MeOH</td>
<td>44</td>
<td>56</td>
</tr>
</tbody>
</table>
From this information, it is apparent that the effects operating in 60, containing the four-membered ring, are also operating in 71. The five-membered ring contains sufficient strain, with subsequent rehybridization of the orbitals at the site of the second ring fusion, to favor electrophilic attack to give the aryl-alpha cation 113.

\[
\begin{array}{c}
\text{X} \\
\end{array}
\]

113

Similarly, silver-ion catalysis of 71 would open to a benzylic cation with an initial partial charge distribution as represented in 114. Any partial positive charge is placed at the more stable aryl-alpha carbon.

\[
\begin{array}{c}
\text{Ag}^+ \\
\text{S+} \\
\text{S+} \\
\text{S+} \\
\end{array}
\]

114

In the meta-fused 73, however, the degree of strain contributed by the second ring fusion has become insignificant, and is no longer a controlling factor. With reduced strain, rehybridization of the bonding orbitals is not required, and there is no stabilizing effect for the
aryl-alpha over the aryl-beta cationic intermediates (Scheme XV). Hence, 73 gives a mixture of products with all reagents.

Scheme XV

The electrophilic substitution reactions of indan and tetralin, conducted by Vaughan and coworkers [63] in 1965, gave similar results. Indan demonstrated a higher degree of selectivity, giving 78% of the product brominated at the aryl-beta position (eq. 47). Tetralin afforded 56% of the beta isomer and 44% of the alpha isomer (eq. 48). Their results were attributed to the greater degree of strain developed in the five-membered ring system [64].

(eq. 47)

78%
The ease of synthesis of these new aneled cyclopropenes \(^\text{67, 69, 71, 73}\) has proven the value of 1-bromo-2-chlorocyclopropene in the synthesis of strained ring systems. In addition, the high regioselectivity of \(^\text{71}\) to electrophiles indicates that such substituted benzocyclopropenes may prove useful as intermediates in the synthesis of substituted aromatic hydrocarbons.
EXPERIMENTAL

General. Please see the Experimental section for 1H-cyclopropa[b]phenanthrene.

6-Bromo-5-(bromomethyl)-2,3-dihydro-1H-indene (90).
The linearly fused indene 67 (10.2 mg, 0.079 mmol) in carbon tetrachloride (3 ml) was cooled to ca. -20°C under nitrogen atmosphere. A solution of bromine (50 mg) in carbon tetrachloride (1 ml) was added in one portion. The reaction was stirred for 5 minutes and warmed to room temperature. The contents were transferred to a separatory funnel, washed with sodium bisulfite solution to destroy excess bromine, washed 1X with water, and dried over magnesium sulfate. The solvent was removed in vacuo to give 90 as a yellow oil (18.7 mg, 82%). NMR 7.42-7.30 (d, 2H), 4.60 (s, 2H), 3.00-2.75 (m, 4H), 2.26-1.90 (m, 2H). Mass spectrum calculated for C_{10}H_{10}^{79}Br_{2}^+: m/e 287.9149; found m/e 287.9143. (Figure 27).

2,3-Dihydro-6-iodo-5-(iodomethyl)-1H-indene (91).
The linearly fused indene 67 (9.6 mg, 0.074 mmol) in carbon tetrachloride (3 ml) was cooled to ca. -10°C under nitrogen atmosphere. A solution of iodine (50 mg) in carbon tetrachloride (1 ml) was added in one portion. The reaction mixture was warmed to room temperature and stirred for 20 minutes. The contents were transferred to a separatory funnel, washed with sodium thiosulfate solution to destroy
excess iodine, washed 2X with water, and dried over magnesium sulfate. The solvent was removed in vacuo to give 91 as a yellow oil (20.4 mg, 72%). NMR 7.64 (s, 1H), 7.33 (s, 1H), 4.55 (s, 2H), 2.95-2.70 (t, 4H), 2.24-1.85 (m, 2H). Mass spectrum calculated for C_{10}H_{16}I_{2}: m/e 383.8872; found m/e 383.8868. (Figure 29).

5-(Chloromethyl)-2,3-dihydro-1H-indene (92).
The linearly fused indene 67 (12.0 mg, 0.092 mmol) and carbon tetrachloride (5 ml) were placed in a flask under nitrogen atmosphere. Concentrated hydrochloric acid (100 microliters) was added, and the mixture stirred vigorously at room temperature for 1 hour. The layers were separated, and the organic phase washed 2X with water and dried over magnesium sulfate. The solvent was removed in vacuo to give 92 as a colorless oil (11.0 mg, 72%). NMR 7.25-7.05 (brt, 3H), 4.58 (s, 2H), 3.05-2.71 (t, 4H), 2.28-1.87 (m, 2H). The spectral data were in accordance with reported values [65]. (Figure 31).

5-(Acetoxyethyl)-2,3-dihydro-1H-indene (93).
Glacial acetic acid (20 microliters) was added to a solution of the linearly fused indene 67 (12.2 mg, 0.094 mmol) in deuterochloroform (0.6 ml) in an NMR tube. The contents were allowed to stand for 3 days, then the NMR of the ring-opened product 93 was recorded. The product was then isolated in 76% yield by removal of the solvent in vacuo. NMR 7.30-7.00
(m, 3H), 5.05 (s, 2H), 3.00-2.71 (t, 4H), 2.30-1.81 (m, 5H).
The spectral data were in accordance with reported values [65]. (Figure 33).

5-(Methoxymethyl)-2,3-dihydro-1H-indene (94).
The linearly fused indene 67 (12.2 mg, 0.094 mmol), carbon
tetrachloride(5 ml), and dry methanol(10 ml) were placed in
a flask. Silver(I) cyanide(3.2 mg) was added, and the
mixture stirred for 1 hour at room temperature. The
solution was diluted with dichloromethane(10 ml) and washed
3X with water, then dried over magnesium sulfate. The
solvent was removed in vacuo to give 94 as a colorless oil
(10.6 mg, 70%). NMR 7.30-6.95 (m, 3H), 4.43 (s, 2H), 3.29
(s, 3H), 3.03-2.76 (t, 4H), 2.24-1.90 (m, 2H). Mass
spectrum calculated for C_{11}H_{14}O: m/e 162.1045; found m/e
162.1046. (Figure 35).

7-Bromo-6-(bromomethyl)-1,2,3,4-tetrahydronaphthalene (95).
The linearly fused 69 (8.5 mg, 0.059 mmol) was reacted with
bromine using the general procedure of 90. Removal of the
solvent in vacuo afforded the dibromide as a yellow oil
(15.2 mg, 85%). NMR 7.56-7.15 (qt, 2H), 4.56 (s, 2H),
2.95-2.56 (brs, 4H), 1.92-1.64 (qn, 4H). Mass spectrum
calculated for C_{11}H_{12}Br_{2}: m/e 301.9306; found m/e
301.9297. (Figure 37).

6-(Chloromethyl)-1,2,3,4-tetrahydronaphthalene (96).
The linearly fused 69 (9.0 mg, 0.063 mmol) was reacted with hydrochloric acid using the general procedure of 92. Removal of the solvent in vacuo afforded 96 as a colorless oil (8.3 mg, 74%). NMR 7.25-6.98 (t, 3H), 4.59 (s, 2H), 2.95-2.60 (brt, 4H), 2.00-1.67 (qn, 4H). The spectral data were in accordance with reported values [65] . (Figure 39).

6-(Acetoxyethyl)-1,2,3,4-tetrahydronaphthalene (97).
The linearly fused 69 (12.2 mg, 0.085 mmol) was reacted with acetic acid using the general procedure of 93. Removal of the solvent in vacuo afforded 97 (12.0 mg, 69%). NMR 7.13-6.87 (m, 3H), 5.03 (s, 2H), 2.91-2.55 (brd, 4H), 2.05 (s, 3H), 1.91-1.55 (m, 4H). The spectral data were in accordance with reported values [65] . (Figure 41).

6-(Methoxymethyl)-1,2,3,4-tetrahydronaphthalene (98).
The linearly fused 69 (8.0 mg, 0.056 mmol) was reacted with methanol and silver ion using the general procedure of 94. Removal of the solvent in vacuo afforded 98 as a colorless oil (7.6 mg, 77%). NMR 7.04 (s, 3H), 4.38 (s, 2H), 3.38 (s, 3H), 2.90-2.59 (m, 4H), 1.92-1.66 (qn, 4H). Mass spectrum calculated for C_{12}H_{16}O: m/e 176.1201; found m/e 176.1201. (Figure 43).

5-Bromo-4-(bromomethyl)-2,3-dihydro-1H-indene (99).
The nonlinearly fused indene 71 (9.2 mg, 0.071 mmol) was reacted with bromine using the general procedure of 90.
Removal of the solvent in vacuo afforded the dibromide as a yellow oil (16.1 mg, 78%). NMR 7.40-6.95 (m, 2H), 4.64 (s, 2H), 3.11-2.79 (m, 4H), 2.30 (m, 2H). Mass spectrum calculated for C_{10}H_{10}Br_{2}: m/e 287.9149; found m/e 287.9143. (Figure 28).

Reaction of 4,5,6-Trihydro-1H-cycloprop[e]indene with Iodine. The nonlinearly fused indene 71 (8.8 mg, 0.068 mmol) was reacted with iodine using the general procedure of 91. Removal of the solvent in vacuo afforded a mixture of the two isomeric ring-cleaved products, the 2,3-dihydro-4-iodo-5-(iodomethyl)-1H-indene 101 and the 5-iodo-4-(iodomethyl)-1H-indene 100 (product ratio 32:68 by NMR). The combined yield was 19.2 mg (74%). NMR 7.6-6.7 (m, 2H), 4.60, 4.51 (2 singlets, corresponding to 100 and 101, 2H), 3.1-2.7 (m, 4H), 2.3-1.9 (m, 2H). Mass spectrum calculated for C_{10}H_{10}I_{2}: m/e 383.8872; found m/e 383.8868. (Figure 30).

5-(Chloromethyl)-2,3-dihydro-1H-indene (102).
The nonlinearly fused indene 71 (10.0 mg, 0.077 mmol) was reacted with hydrochloric acid using the general procedure of 92. Removal of the solvent in vacuo afforded 102 as a colorless oil (12.8 mg, 68%). NMR 7.25-7.05 (brt, 3H), 4.58 (s, 2H), 3.05-2.71 (brt, 4H), 2.28-1.85 (m, 2H). The spectral data were in accordance with reported values [65]. (Figure 32).
5-(Acetoxyethyl)-2,3-dihydro-1H-indene (103).

The nonlinearly fused indene 71 (9.8 mg, 0.075 mmol) was reacted with acetic acid using the general procedure of 93. Removal of the solvent in vacuo afforded the ester as a colorless oil (1.0.1 mg, 71%). NMR 7.30-7.00 (m, 3H), 5.05 (s, 2H), 3.00-2.71 (t, 4H), 2.30-1.81 (m, 5H). The spectral data were in accordance with reported values [65]. (Figure 34).

5-(Methoxymethyl)-2,3-dihydro-1H-indene (104).

The nonlinearly fused indene 71 (11.2 mg, 0.086 mmol) was reacted with methanol and silver ion using the general procedure of 94. Removal of the solvent in vacuo afforded the ether as a colorless oil (10.5 mg, 75%). NMR 7.30-6.95 (m, 3H), 4.43 (s, 2H), 3.29 (s, 3H), 3.03-2.76 (t, 4H), 2.24-1.90 (m, 2H). Mass spectrum calculated for C_{11}H_{14}O: m/e 162.1045; found m/e 162.1046. (Figure 36).

Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]naphthalene With Bromine. The nonlinearly fused 73 (10.2 mg, 0.071 mmol) was reacted with bromine using the general procedure of 90. Removal of the solvent in vacuo afforded a mixture of the two ring-cleaved products, the 5-bromo-6-(bromomethyl)-1,2,3,4-tetrahydronaphthalene 106 and the 6-bromo-5-(bromomethyl)-isomer 105 (product ratio 20:80 by NMR). The combined yield was 17.2 mg (80%). NMR 7.40-6.84 (m, 2H), 4.68, 4.65 (2 singlets, corresponding to 105 and
106, 2H), 3.00-2.60 (brqn, 4H), 2.04-1.60 (m, 4H). Mass spectrum calculated for C_{11}H_{12}^{79}Br_{2}: m/e 301.9306; found m/e 301.9297. (Figure 38).

Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]naphthalene With HCl. The nonlinearly fused 73 (13.0 mg, 0.090 mmol) was reacted with hydrochloric acid using the general procedure of 92. Removal of the solvent in vacuo afforded a mixture of the two ring-cleaved products, the 5-(chloromethyl)-1,2,3,4-tetrahydronaphthalene 107 and the 6-(chloromethyl)-isomer 108 (product ratio 45:55 by NMR). The combined yield was 11.7 mg(72%). NMR 7.20-6.94 (m, 3H), 4.59, 4.52 (2 singlets, corresponding to 107 and 108, 2H), 3.00-2.60 (m, 4H), 2.00-1.68 (m, 4H). The spectral data were in accordance with reported values [65]. (Figure 40).

Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]naphthalene With Acetic Acid. The nonlinearly fused 73 (11.6 mg, 0.081 mmol) was reacted with acetic acid using the general procedure of 93. Removal of the solvent in vacuo afforded a mixture of the two ring-cleaved products, the 5-(Acetoxy)methyl)-1,2,3,4-tetrahydronaphthalene 109 and the 6-(Acetoxy)methyl)-isomer 110 (product ratio 33:67 by NMR). The combined yield was 10.8 mg(66%). NMR 7.18-7.00 (d, 3H), 5.08, 5.03 (2 singlets, corresponding to 109 and 110, 2H), 2.95-2.62 (m, 4H), 2.08 (s, 3H), 1.94-1.65 (m, 4H). The
spectral data were in accordance with reported values [65]. (Figure 42).

Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]naphthalene With Methanol. The nonlinearly fused 73 (10.0 mg, 0.069 mmol) was reacted with methanol and silver ion using the general procedure of 94. Removal of the solvent in vacuo afforded a mixture of the two ring-cleaved products, the 5-(methoxymethyl)-1,2,3,4-tetrahydronaphthalene 111 and the 6-(methoxymethyl)-isomer 112 (product ratio 44:56 by NMR). The combined yield was 8.8 mg (72%). NMR 7.20–6.96 (m, 3H), 4.43, 4.40 (2 singlets, corresponding to 111 and 112, 2H), 3.41, 3.39 (2 singlets, 3H), 2.94–2.60 (m, 4H), 2.00–1.62 (m, 4H). Mass spectrum calculated for C_{12}H_{16}O: m/e 176.1201; found m/e 176.1201. (Figure 44).
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6. The early data and predictions have been shown to be ambiguous. See: G.M. Badger, Quart. Rev. Chem. Soc., 5, 147 (1951).


16. E. Vogel and B. Halton, personal communication, see ref. 1.


28. W.E. Billups and L.E. Reed, unpublished observations, see ref. 1.


49. I thank Dr. Terry Marriott for the high-resolution mass spectral studies.


58. The compound was obtained commercially.

59. W.E. Billups, W.Y. Chow, D. Wolf, and C.V. Smith, unpublished observations, see ref. 1.


APPENDIX

SPECTRA
Figure 3a

Figure 3b
Figure 4a

Figure 4b
Figure 22a

Figure 22b