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SYNTHESIS OF METHYLENECYCLOPROPENE, 1H-
CYCLOPROP(B)ANTHRACENE AND A STUDY OF THE
DEHYDROCHLORINATION OF AROMATIC GEM-
DICHLOROCYCLOPROGANES

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SYNTHESIS OF METHYLENECYCLOPROPENE,
1H-CYCLOPROP[1]ANTHRACENE AND A
STUDY OF THE DEHYDROCHLORINATION OF AROMATIC
gem-DICHLOOROCYCLOPROANES

by

EDWARD W. CASSERLY

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

W. E. Billups
W. E. Billups, Professor of Chemistry
Chairman

E. S. Lewis
E. S. Lewis, Professor of Chemistry

L. V. McIntire, Professor of Chemical Engineering

Houston, Texas

May, 1984
Synthesis of Methylene cyclopropene, 1H-Cycloprop[b]anthracene

and a Study of the Dehydrochlorination of Aromatic

gem-Dichlorocyclopropanes

by

Edward W. Casserly

Abstract

Methylene cyclopropene was generated under two different reaction conditions. The passage of 2-chloromethylene cyclopropene through a vertical column containing potassium tert-butoxide supported on Chromosorb W (45/60 mesh) at 240°C and 10 mtorr produced methylene cyclopropene nearly free of impurities. The nuclear magnetic resonance spectra (¹H and ¹³C) were obtained at -100°C in tetrahydrofuran-d₈. The exocyclic protons appeared at δ 3.47 (t, J=2.2 Hz) and the ring protons at δ 8.61 (t, J=2.2 Hz). The exocyclic carbon appeared at δ 59.57 (t, ¹JCH=161.5 Hz) and the ring carbons at δ 132.90 (t, ¹JCH=228.5 Hz). The quaternary carbon was not observed. The infrared spectrum was obtained on an IBM Model 98 FTIR. The characteristic high energy transition appeared at 1770.3 cm⁻¹. These spectra indicate that ¹a contributes significantly to the resonance hybrid.
Methylene cyclopropene was also generated and trapped in a second flask as a Diels-Alder adduct when 2-bromomethylene cyclopropane was injected into a hot solution (75°C) of potassium tert-butoxide in dimethyl sulfoxide and the volatiles trapped in a second flask containing cyclopentadiene.

A series of aromatic gem-dichlorocyclopropanes, precursors to the cycloproparenes, were eliminated by potassium tert-butoxide in dimethyl sulfoxide in the presence of methyl mercaptide. The major products were the (thiomethyl)methylnaromatics. The failure to trap the expected cyclopropanes is seen as evidence of the reaction proceeding via a different mechanism in the higher homologs. This necessitated the development of a synthetic sequence in which the leaving groups were positioned at the bridge-head carbons.

1H-Cycloprop[b]anthracene was synthesized via this new synthetic sequence which involves the Diels-Alder reaction of 1-bromo-2-chlorocyclopropane. The treatment of 1a-bromo-9a-chloro-1a,2,9,9a-tetrahydro-1H-cycloprop[b]anthracene with potassium tert-butoxide in tetrahydrofuran at -78 to -30°C afforded 1H-cycloprop[b]anthracene in 41.5% yield. The absence of unusual spectral properties (1H NMR, 13C NMR, UV, IR) indicates that it does not possess any great degree of bond fixation.
Acknowledgements

I would like to thank Dr. W. E. Billups for his guidance and inspiration during my years as a graduate student. I would also like to thank my fellow graduate students for their friendship and their timely discussions during the course of my research, especially L.-J. Lin, W. A. Rodin, B. E. Arney, Jr., and D. Hamp.

The love and support of my entire family, especially my parents and my wife, Ricci, have made this thesis enjoyable and worthwhile.

The financial support of Rice University in the form of a Rice Fellowship and the Robert A. Welch Foundation in the form of a Predoctoral Fellowship are also gratefully acknowledged.
To Ricci
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AND THE SYNTHESIS OF 1H-CYCLOPROP[b]ANTHRACENE

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Synthesis of Methylene cyclopropene
INTRODUCTION

Methylenecyclopropene (1) as the simplest cross-conjugated cyclic system, has attracted the attention of chemists, both for its theoretical interest and the synthetic challenge.\(^1\),\(^2\) There exists ten possible isomers of \(\text{C}_4\text{H}_4\), however, only three are known: but-1-yn-3-ene (2), butatriene (3), and 1,3-cyclobutadiene (4).

\[ \begin{array}{cccc}
1 & 2 & 3 & 4 \\
\text{ } & \text{ } & \text{ } & \text{ }
\end{array} \]

\[ \begin{array}{cccc}
5 & 6 & 7 & 8 \\
\text{ } & \text{ } & \text{ } & \text{ }
\end{array} \]

\[ \begin{array}{cccc}
9 & 10 & 11 & 12 \\
\text{ } & \text{ } & \text{ } & \text{ }
\end{array} \]

Of these, only 2 and 3 are isolatable and 4 is seen only in low temperature matrices. Methylenecyclopropene has been calculated to be the third most stable \(\text{C}_4\text{H}_4\) hydrocarbon (Table I).

The need to incorporate three \(sp^2\)-hybridized carbons in a three-membered ring should induce considerable strain. Indeed, the strain energy of 1 has been calculated to be 58.1 Kcal/mol and the heat of formation to be 79.1 Kcal/mol.\(^4\) However, methylenecyclopropene has a possible charge-separation resonance structure 1a which has been
Table I

Theoretical Relative Energies (Kcal/mol)$^3$

<table>
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<tr>
<th>Molecule</th>
<th>4-31G</th>
<th>6-31G$^*$</th>
</tr>
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<tbody>
<tr>
<td>But-1-yn-3-ene (2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Butatriene (3)</td>
<td>11.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Methylene cyclopropene (1)</td>
<td>36.2</td>
<td>23.6</td>
</tr>
<tr>
<td>1,3-Cyclobutadiene (1)$^2_A^2g$ (4)</td>
<td>45.7</td>
<td>35.4</td>
</tr>
<tr>
<td>1,3-Cyclobutadiene (1)$^1A^1g$ (4)</td>
<td>51.3</td>
<td>41.3</td>
</tr>
<tr>
<td>Tetrahedrane (5)</td>
<td>93.8</td>
<td>68.5</td>
</tr>
<tr>
<td>1,2-Cyclobutadiene (6)</td>
<td>78.2</td>
<td>73.1</td>
</tr>
<tr>
<td>Bicyclo[1.1.0]butene $^1,3$ (7)</td>
<td>117.0</td>
<td></td>
</tr>
<tr>
<td>Cyclobutyne (8)</td>
<td>117.5</td>
<td></td>
</tr>
<tr>
<td>Methylcyclopropyne (9)</td>
<td>132.8</td>
<td></td>
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calculated to contribute minor resonance energy stabilization (0.96 $\beta$).\textsuperscript{5} The possible contribution of this zwitterionic form is further indicated by other theoretical calculations. The calculated dipole moment is 2.08 D in the direction of the exocyclic double bond indicating considerable polarization.\textsuperscript{3} The $\pi$-electron density is calculated as follows:\textsuperscript{3}

\[
\begin{array}{c}
\text{1.216} \\
0.954 \\
0.915
\end{array}
\]

The bond lengths which are calculated as shown,\textsuperscript{3,6,7} are very similar to those of the cyclopropenyl cation\textsuperscript{3} and cyclopropenone.\textsuperscript{3}

\[
\begin{array}{ccc}
1.303\text{A} & 1.318\text{A} & 1.306\text{A} \\
1.444\text{A} & 1.468\text{A} & 1.429\text{A} \\
1.305\text{A} & 1.348\text{A} & 1.322\text{A}
\end{array}
\]

\[
\begin{array}{c}
1.377\text{A} \\
1.412\text{A} \\
1.302\text{A}
\end{array}
\]
These calculations suggest that the contribution of 1a to the resonance hybrid of 1 may be significant, indeed.

Stable methylenecyclopropanes have been synthesized by employing substituents which stabilize resonance form 1a. Strong electron-withdrawing groups such as CN, CF₃, and F have been used successfully to prepare stable derivatives of methylenecyclopropane: 8-11

A second method of stabilizing unstable species is by steric shielding by bulky groups, e.g. the t-butyl group. Tri-t-butylcyclobutadiene is stable at room temperature for less than one day in solution.12 This same approach was used by Blakeney13 and by Lin14 in this laboratory to prepare unstable yet isolable substituted methylenecyclopropanes 15 and 16, and 17 respectively.
Methylenecyclopropenes exhibit characteristic spectral properties. The infrared spectra of substituted methylenecyclopropenes exhibit two characteristic bands. A high energy vibration in the region of 1810 to 1880 cm\(^{-1}\), is attributed to a ring vibration. A second band in the region 1510 to 1550 cm\(^{-1}\) is assigned to the exocyclic double bond vibration.\(^\text{15}\)

The \(^1\)H NMR spectra of substituted methylenecyclopropenes exhibit
dramatic shifts, indicative of significant contribution from resonance forms of type 1a (the chemical shifts are given in ppm).\textsuperscript{13-1b}

The ultraviolet spectrum of substituted methylenecyclopropenes are necessarily complex due to the presence of phenyl substituents or of conjugated chromophores at C-4. The ultraviolet maxima of some substituted methylenecyclopropenes are dependent on solvent polarity and hydrogen bonding effects.\textsuperscript{15} The predicted \( \pi \rightarrow \pi^* \) transition for 1, using M.O. calculations, is 198 nm.\textsuperscript{17}

The first attempt to prepare 1 was by Krull and co-workers in 1971.\textsuperscript{18} Photolysis and flash vacuum pyrolysis of cis-1-methylenecyclopropene-2,3-dicarboxylic anhydride (20) yielded only vinyl acetylene (2) (Scheme I). The intermediacy of 1 was not established. A plausible alternative sequence is the formation of the diradical (21), a facile process for methylenecyclopropanes.

Chapman\textsuperscript{19} also used a photolytic method in his attempt to synthesize 1. Photolysis of methylenecyclobutanone (22) in an argon matrix at 8 K produced only the allene-ketene (23) (Scheme II). At shorter wavelengths, 23 decarbonylates to presumably yield butatriene (3) and methylenecyclopropene (1) which give vinylacetylene (2) and acetylene on further irradiation. The intermediacy of 1 was not established.
Scheme I

1

20

21

\[ \cong - \equiv \]

2
Scheme II

\[
\begin{align*}
\text{22} & \xrightarrow{hv \atop 8 \text{ K}} \text{23} \\
\text{23} & \xrightarrow{hv} \text{[CH}_2\text{C} \equiv \text{CH]} \\
\text{2} & \xrightarrow{hv} \text{1} \\
\text{1} & \xrightarrow{hv} \text{[CH}_2\text{C} \equiv \text{CH]} \\
\text{3} & \xrightarrow{hv} \text{H}_2\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \\
\text{3} & \xrightarrow{hv} \text{HC} \equiv \text{CH}
\end{align*}
\]
Shields and Gardner\textsuperscript{20} employed a dehydrochlorination-isomerization sequence of 1,1-dichloro-2-methylcyclopropane (24) which produced only polymer (Scheme III).

Scheme III

\[ \begin{align*}
\text{C} & \rightarrow \text{C} \\
\text{Cl} & \rightarrow \text{Cl} \\
\text{Cl} & \rightarrow \text{Cl}
\end{align*} \]

\[ \text{polymer} \]

The intermediacy of \text{1} has been established by trapping experiments with nucleophiles and cyclopentadiene. Billups and co-workers\textsuperscript{21,22} in the base induced elimination of 1,2-dichloro-1-methylcyclopropane (25) trapped the intermediate \text{1} with nucleophiles giving \text{26} and \text{27} (Scheme IV). Of course, the pathway does not necessarily have to involve \text{1}.
Scheme IV

Oxidation of sulfide (27) to the sulfone followed by elimination afforded 26 via the intermediate 1.

Further evidence for the intermediacy of 1 is derived by the "in situ" Diels-Alder trapping reported by Weber and Neuenschwander. Base-induced elimination of the sulfonium salt (28) in the presence of cyclopentadiene afforded a 10% yield of the endo-Diels-Alder adduct (29) (Scheme V). The evidence indicates that 1 is relatively stable, but extremely reactive intermediate. It is long-lived enough to experience trapping by nucleophiles and dienes, but it is too unstable to be isolated by ordinary methods.
Scheme V

\[
\text{Me-S-Ph}^+ + \text{Na}^+ \text{BF}_4^- + \text{C}_5H_6^- \rightarrow \text{THF} \rightarrow \left[ \text{cyclopropenylidene} \right]^{-1} \\
+ \text{C}_5H_6 \rightarrow \text{product} \]

28 \sim 29
RESULTS AND DISCUSSION

Once the intermediacy of 1 had been firmly established, work in this laboratory concentrated on demonstrating the stability of methylenecyclopropene by transference in vacuo (i.e. generation in one flask and trapping in a second) and ultimately on the isolation of 1. The ideal precursor to 1 appeared to be the monohalides (30) or (31).

![Chemical Structures](image)

The simplest method of preparing 30 involved the addition of monobromocarbene to allene. Thus, 30 was prepared in low yield by the method of Martel and Hiriart\(^\text{24,25}\) (eq. 1). However, purification

\[
\text{CH}_2=\text{C}=\text{CH}_2 + \text{CH}_2\text{Br}_2 \xrightarrow{\text{NaN[Si(CH}_3)_3]_2, -30^\circ\text{C}} \text{Br} \quad \text{(eq. 1)}
\]

involved tedious preparative gas chromatography. Initial work utilized this precursor. Compound 31 was later prepared, again in low yield (ca. 7%), by the method of Closs and Closs\(^\text{26}\) (eq. 2).
\[ \text{CH}_2=\text{C}==\text{CH}_2 + \text{CH}_2\text{Cl}_2 \xrightarrow{\text{MeLi}, -10^\circ\text{C}} \text{Cl} \] (eq. 2)

Purification of this compound could be achieved by careful distillation at atmospheric pressure (b.p. 68-72^\circ\text{C}). The latter part of this work utilized this precursor.

Elimination of bromide (30) with potassium \&-butoxide in tetrahydrofuran or dimethyl sulfoxide yielded the corresponding \&-butyl ether (26). In the presence of external nucleophile, methyl mercaptide, the corresponding methyl sulfide (27) was also produced. Both 26 and 27 were identical to the known compounds. These results implied the intermediacy of 1 as an \( S_N^2 \) displacement on cyclopropanes is unprecedented. Attempts to trap the intermediate 1 "in situ" with cyclopentadiene yielded only 26. This would imply that 1 is trapped by nucleophiles faster than it is trapped by dienes. In the absence of nucleophiles Weber and Neuenschwander successfully trapped 1 with cyclopentadiene.

Denis and co-workers have developed two methods of preparing unstable alkenes. One involved the elimination of the halide in hot dimethyl sulfoxide under vacuum. Thus, spiropentene (32) was synthesized from the corresponding bromo-spiropentane (33) (eq. 3).
Potassium $\epsilon$-butoxide in dimethyl sulfoxide was slowly added to a hot (90$^\circ$C) solution of 33 in dimethyl sulfoxide at 80 mm Hg. Spiropentene was distilled from the solution as it was formed. Attempts to utilize this method were marginally successful. Due to the volatility of bromide (30), the addition sequence was reversed. A solution of 30 in dimethyl sulfoxide was quickly added to a hot (55 to 75$^\circ$C) solution of potassium $\epsilon$-butoxide in dimethyl sulfoxide under vacuum. Any volatile products were collected in a cold trap containing cyclopentadiene. Other conditions were also investigated, e.g. dimethyl sulfoxide at ambient temperature, tetrahydrofuran at -50$^\circ$C, pressures from 0.1 to 80 mm Hg, and both continuous and static vacuums. In some cases, two or three isomeric C$_9$H$_{10}$ products were identified by GC/MS and $^1$H NMR. These products were the endo-isomer (29) (identical to that reported by Weber and Neuenschwander$^{23}$), the exo-isomer (34) (identical to that prepared by an alternate route described below), and a rearranged product (35) (identical to that prepared independently from 34). Neither 34 nor 35 were reported by Weber and Neuenschwander$^{23}$ In the case of the reaction at 75$^\circ$C at 0.1 mm Hg (see experimental), two minor products were identified by GC/MS in addition to the major product, 26.
Preparative gas chromatography afforded a mixture of the two \( C_{9}H_{10} \) isomers, \(~26\), and dicyclopentadiene. The major \( C_{9}H_{10} \) product was the rearranged isomer \(~35\) and the minor \( C_{9}H_{10} \) product was the exo-isomer \(~34\). No endo-isomer \(~29\) was seen, although rearrangement during purification was most probable.

The exo-isomer \(~34\) was compared to that prepared by the alternate route. The chloromethyl carbene\(^{29,30}\) adduct with norbornadiene was easily dehydrochlorinated with potassium \( t\)-butoxide in dimethyl sulfoxide (Scheme VI).

\( \text{Scheme VI} \)

\[ \text{Pathway Diagram} \]

It was later found that both the endo- and the exo-isomer rearrange on heating to \(~35\) \(^{31}\) (Scheme VII).
Scheme VII

The second method of preparing unstable alkenes developed by Denis and co-workers involved the dehydrohalogenation of the appropriate halide by potassium tert-butoxide supported on Chromosorb W at high temperatures and under vacuum. The temperatures used were in the range of 100 to 160°C and the pressure was 0.02 mm Hg. Cyclopropyl bromide was used as a model compound to maximize the reactions conditions. This compound was used by Denis to prepare cyclopropene in high yields (75% on an analytical, e.g. 50 mg, scale). A variety of conditions were tried and the cyclopropene-cyclopentadiene Diels-Alder adduct identified by GC/MS. The temperatures/pressures employed were: 160°C at 0.5 to 1.0 mm Hg, 180°C at 0.1 mm Hg, and 100°C at 0.3 mm Hg. Under these conditions, a large quantity of product was formed, although no quantified yields were obtained. The elimination reaction
appeared independent of both temperature and pressure. All attempts to
form 1 under the same conditions failed. No Diels-Alder adducts were
formed, the only identified product being the \( \varepsilon \)-butyl ether (26).

While these and other approaches were being attempted, L.-J. Lin
in this laboratory prepared the chloride 31. The treatment of 31
with potassium \( \varepsilon \)-butoxide in tetrahydrofuran at \(-40^\circ C\) under vacuum (0.5
mm Hg) and the volatiles collected in a cold trap (liquid \( N_2 \))
containing cyclopentadiene afforded the Diels-Alder adduct \( \text{29}^{23} \) in 6%
yield. These conditions were a combination of those used in his
synthesis\(^{14} \) of 17 and those used to synthesize 1 from the bromide (30).
As the chloride appeared to be the better precursor, our approaches
were joined and our efforts concentrated on 31.

The \(^1\text{H NMR} \) spectrum of methylenecyclopentene was first obtained by
the elimination of 31 with potassium \( \varepsilon \)-butoxide in tetrahydrofuran-\( d_8 \)
at \(-40^\circ C\) under 0.5 mm Hg vacuum. The volatiles were instantly
collected in an NMR tube cooled by liquid \( N_2 \). The spectrum, taken at
\(-100^\circ C\), showed methylenecyclopentene (10% of the volatiles) exhibiting
triplets (J=2.2 Hz) at \( \delta \) 8.61 (ring protons) and 3.47 (exocyclic double
bond protons), the \( \varepsilon \)-butyl ether (26) (10% of the volatiles) and
starting chloride (80% of the volatiles). Compound 1 decomposed above
\(-75^\circ C\), affording unidentified products. This proved to be a viable
method for producing 1, however, it was plagued by low yields and a
large quantity of impurities. Efforts were then re-shifted to the
supported base method of Denis.
It was apparent that the initial model studies using cyclopropyl bromide were non-applicable to the synthesis of 1. Hence, the apparatus was redesigned (see Figure 1). A short wide vertical tube, replacing the long narrow horizontal tube, was used to reduce the contact time and decrease the formation of 26. In addition, a vertical tube was easier to pack and handle. A better vacuum system, capable of 0.01 mm Hg was employed, again to reduce the contact time. A series of U-traps were designed to trap unreacted 31, 26, and any #butanol formed. The precursor was introduced at a very slow rate (100 ul/hour). The ideal temperature was found to be ca. 240°C.

In a typical experiment (eq. 4), the reaction tube (21 cm X 3.5 cm with a 34/45 ground-glass joint at the top and a 14/20 joint at the bottom) was loaded with 6 cm of glass wool, 3 cm of Chromosorb W, 4 cm of potassium #butoxide on Chromosorb W, and 2 cm of Chromosorb W (the extra Chromosorb W was used due to the fact that potassium #butoxide sublimes off of the support). The entire apparatus was placed under vacuum (0.01 mm Hg) and the portion of the tube containing the Chromosorb W was heated to 240°C by means of a heating tape. The temperature was measured by a thermocouple inserted in a small tube placed between the reaction tube and the heating tape. There was a series of four traps, the first two cooled by dry ice/acetone baths and the latter two by liquid N₂ baths. Once the system had equilibrated, the rate of addition of 31 was controlled by cooling the flask containing 31 to ca. -50°C.
Figure 1.
For Diels-Alder trapping experiments, cyclopentadiene was introduced into the first liquid \( \text{N}_2 \) cooled trap before and/or after the reaction. After the reaction, nitrogen was introduced and the liquid \( \text{N}_2 \) bath replaced by a dry ice/acetone bath which was allowed to warm to room temperature.

For NMR studies, tetrahydrofuran-\( \text{d}_8 \) was introduced into the first liquid \( \text{N}_2 \) cooled trap to which an NMR tube was attached. After the reaction, the trap was closed off from the vacuum pump and the cold bath warmed to ca. \(-100^\circ \text{C}\) (pentane/liquid \( \text{N}_2 \)). After the solution collected in the NMR tube, the tube was sealed. The \(^1\text{H NMR}\) and \(^{13}\text{C NMR}\) spectra were then recorded at ca. \(-100^\circ \text{C}\).

The \(^1\text{H NMR}\) spectrum in tetrahydrofuran-\( \text{d}_8 \), exhibits the same triplets as described above. The exocyclic protons (\(\delta 3.47\)) exhibit a large upfield shift (1.93 ppm) relative to the exocyclic protons of methylenecyclopropane which appear at \(\delta 5.40\). The ring protons (\(\delta 8.61\)) exhibit a corresponding large downfield shift (1.60 ppm) relative to the ring protons of cyclopropene which appear at \(\delta 7.01\). The \(^{13}\text{C NMR}\) spectrum displays the same effect. The exocyclic carbon appears at \(\delta 59.57\) (\(^{1}J_{\text{CH}}=161.5\ \text{Hz}\)) and the two ring carbons at \(\delta 132.90\)
$^{1}J_{\text{CH}}=228.5$ Hz. The quaternary carbon was not identified. The exocyclic carbon is again shifted 43.49 ppm upfield relative to that in methylenecyclopropane which appears at $\delta$ 103.06. The ring carbons were shifted 24.2 ppm downfield relative to those in cyclopropene which appear at $\delta$ 108.7. It is well documented that $^{13}$C shifts of negative ions correlate with the electron density at that carbon. The increased electron density causes electronic repulsion, the orbitals expand and the carbon is more shielded. The carbon is then seen further upfield. Positive ions react in the opposite manner since deshielding results from electron deficiency. However, the more the positive charge is dispersed, as by resonance, the electron deficient carbon becomes more shielded. With this understanding, the above $^{13}$C shifts (as well as the $^{1}$H shifts) suggest that $\alpha$ contributes significantly to the resonance hybrid of methylenecyclopropane.

The infrared spectrum of 1 was obtained by trapping 1 in a liquid $\mathrm{N}_{2}$ cooled U-trap. The trap was then attached to an IBM Model 98 FTIR spectrometer. Methylenecyclopropane was slowly introduced by carefully warming the trap. The spectrometer operated at a pressure in the order of $10^{-6}$ mm Hg. Methylenecyclopropane was condensed, along with a large quantity of argon onto a polished copper surface cooled to 15 K with a closed cycle helium refrigerator. Several spectra, corresponding to different copper surfaces, were obtained. The cold trap temperature was increased at $10^{{\circ}}$C intervals from -120 to $-80^{{\circ}}$C during this operation. The different copper surfaces corresponded to
different temperatures. In this fashion, concentration studies could be performed and any impurities could be subtracted. The only known impurity was isobutylene formed from the basic dehydration of γ-butenol. A higher boiling unknown impurity was also subtracted. The concentration study showed that the five strongest peaks arise from methylenecyclopropene. The weak absorptions could not be positively associated with methylenecyclopropene. The high energy transition which appears in the region 1810 to 1880 cm⁻¹ in substituted compounds, is shifted to 1770.3 cm⁻¹ in the parent compound. This is consistent with the la resonance structure. As a detailed analysis of the infrared spectrum has not yet been performed, the other prominent bands could not be assigned. Photolysis of the matrix through a quartz window using a mercury lamp for 10 min led to a disappearance of the bands associated with la.

Samples of la for mass spectral studies were collected in a similar fashion. Low resolution mass spectrometry at 20 to 70 ev displays a base parent peak at m/e 52 with a major fragment at m/e 39. A spectrum of pure la could not be obtained due the presence of isobutylene (m/e 56). Elemental composition was determined by high resolution mass spectrometry; calculated for C₄H₄: m/e 52.0313, found m/e 52.0312.

The data conclusively demonstrates that methylenecyclopropene is not only a reactive intermediate, but a semi-stable compound whose properties can be determined. The use of Denis' supported base
apparatus has proven to be a viable route for generating analytical quantities (15-25 mg) of this reactive hydrocarbon. Further scale-up to 100 mg or more appears quite feasible which will allow the chemistry of methylenecyclopropene to be studied on a preparative scale.
EXPERIMENTAL

General. Proton magnetic resonance spectra were recorded using a Varian Model EM-390 (90 MHz) or a JEOL FX90Q (90 MHz) spectrometer. $^{13}\text{C}$ NMR spectra were recorded on a JEOL FX90Q (22.63 MHz) spectrometer. Chemical shifts ($\delta$) are expressed in ppm downfield from TMS. Unless otherwise noted, NMR spectral data were obtained as a chloroform-$d_1$ solution. Infrared spectra were recorded on a Beckman IR 4230 spectrometer as solutions in carbon tetrachloride and carbon disulfide. Ultraviolet spectra were recorded in hexane solution on a Cary 17 spectrometer. High resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer, and low resolution mass spectra were recorded on a Finnigan Model 3300 gas chromatograph/mass spectrometer operated at 30 ev. A Hewlett Packard Model 700 gas chromatograph with a thermal conductivity detector and operated at a flow rate of 60 cc of helium per minute was used for all analytical and preparative gas chromatography. All melting points and boiling points are uncorrected.

Tetrahydrofuran was distilled from sodium-benzophenone ketal prior to use. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure prior to use. Column chromatography was performed on Baker reagent grade silica gel (60-200 mesh). Merck precoated silica gel plates were used for analytical (100 X 50 X 0.25 mm) and preparative (200 X 200 X 2 mm) thin layer chromatography. All other chemicals were of reagent quality and used as obtained from the
manufacturers. All reactions were carried out in an inert atmosphere (dry nitrogen) where necessary.

2-Bromomethylenecyclopropane (30). Allene (20.4 g, 11.4 ml, 0.5 mol) was added to a slurry of sodium bis-trimethylsilyl amide (18.7 g, 0.1 mol) and pentane (250 ml) cooled to -78°C. The mixture was warmed to -30 to -40°C and dibromomethane (17.7 g, 7.14 ml, 0.1 mol) was added via syringe over 30 min. After stirring for 1.5 hours at -30°C, the mixture was stirred for 2 hours at -10°C, and then allowed to warm to room temperature.

The volatiles were removed under vacuum. The solution was concentrated to 50-75 ml at atmospheric pressure, then the bis-trimethylsilyl amine was decomposed by stirring with methanol (3 eq) at 40°C. The mixture was washed with water (2X), brine (1X), and dried over MgSO₄. The mixture was distilled at atmospheric pressure. Dibromomethane and 30 distill off together at 90-100°C. The distillate was then purified by preparative gas chromatography (10% FFAP on Chromosorb W AW/DMCS). ¹H NMR (CDCl₃) δ 1.32-2.0 (m, 2H), 3.36-3.6 (m, 1H), 5.56-5.72 (m, 1H), and 5.72-5.92 (m, 1H). ¹³C NMR (CDCl₃) δ 13.30, 15.15, 108.66, 131.0 Mass spectrum calculated for C₄H₅Br: m/e 131.9574, 133.9554; found m/e 131.9574, 133.9550.

2-Chloromethylenecyclopropane (31). Allene (30 ml, 23.6 g, 0.5 mol) was added to a 1-1 flask equipped with a large liquid N₂ condenser, two
addition funnels and a magnetic stirrer cooled to \(-78^\circ\text{C}\). The condenser
was cooled to \(-130^\circ\text{C}\) (pentane/liquid \(N_2\)). The flask was warmed to
\(-10^\circ\text{C}\) and methyl lithium (1.6M, 400 ml, 0.64 mol) and \(\text{CH}_2\text{Cl}_2\) (70 ml,
93g, 1.1 mol) were added dropwise in an equal molar fashion (i.e. MeLi
was added five times faster than the \(\text{CH}_2\text{Cl}_2\)). After the addition was
completed (ca. 2 hours), the mixture was stirred for an additional 30
min and then allowed to warm to room temperature. The flask was then
cooled to 0\(^\circ\text{C}\) and water was added slowly. The layers were separated
and the aqueous phase extracted with ether (2X). The combined organics
were washed with water (1X), brine (1X) and dried over MgSO\(_4\). The
majority of the solvent was removed by careful distillation through a
packed (glass helices) column (25 cm). The concentrate (100 ml) was
rapidly distilled through a regular distilling apparatus and the
residue vacuum distilled (0.1 mm Hg). The vacuum distilled residue
contained a significant amount of product and was added to the
distillate. The remaining solvent was distilled through the packed
column. The final concentrate was distilled through a vigreux column
(9 cm), b.p. 68-72\(^\circ\text{C}\), 3.56 g, ca. 7\% yield. \(^1\text{H NMR (CDCl}_3\text{)}\) \(\delta\) 0.70-1.90
(m, 2H), 3.40-3.60 (m, 1H), 5.56-5.64 (m, 1H), 5.76-5.90 (m, 1H). \(^{13}\text{C NMR (CDCl}_3\text{)}\) \(\delta\) 14.96, 27.00, 108.42, 131.05. Mass spectrum calculated
for \(\text{C}_4\text{H}_7\text{Cl}\): m/e 88.0080, 90.0050; found m/e 88.0078, 90.0051.

Reaction of 30 with potassium \(t\)-butoxide in tetrahydrofuran. A
solution of 30 (53.7 mg, 0.40 mmol) in tetrahydrofuran (1 ml) was added
via syringe to a stirred slurry of potassium tert-butoxide (272 mg, 2.4 mmol) in tetrahydrofuran (4 ml). The mixture was stirred for 1 hour at room temperature. Water was then added and the aqueous layer extracted with pentane (4X). The combined organics were washed with water (4X), brine (1X), dried over MgSO₄ and the solvent removed by careful distillation. GC and GC/MS analysis indicated only one product, 26, as compared to an authentic sample.

Reaction of 30 with potassium tert-butoxide and methyl mercaptide in dimethyl sulfoxide. A mixture of potassium tert-butoxide (252 mg, 2.25 mmol) and methyl mercaptan (54 mg, 1.13 mmol) in dimethyl sulfoxide (3 ml) was prepared by distilling the previously condensed methyl mercaptan through the potassium tert-butoxide solution. A solution of 30 in dimethyl sulfoxide (1 ml) was added dropwise via syringe with stirring. The mixture was stirred for 1.5 hours at room temperature. Water was then added and the aqueous layer extracted with pentane (4X). The combined organics were washed with water (4X), brine (1X), dried over MgSO₄ and the solvent removed by careful distillation. GC and GC/MS analysis showed two products, 26 and 27 in a ratio of 4 to 1 as compared to authentic compounds.

Reaction of 30 with potassium tert-butoxide in dimethyl sulfoxide under vacuum. A solution of 30 (1.0 g, 7.5 mmol) in dimethyl sulfoxide (2 ml) was added via syringe to a hot (75°C) solution of potassium
$\tau$-butoxide (1.3 g, 11.3 mmol) in dimethyl sulfoxide (20 ml) under vacuum (0.1 mm Hg). Any volatiles were collected in a cold trap containing cyclopentadiene (5 g, 75 mmol). The reaction was immediate. Nitrogen was introduced to the system and the cold pot was allowed to warm to room temperature with stirring. Excess cyclopentadiene was removed in vacuo. The residue was taken up in pentane, washed with water (1X), brine (1X), dried over MgSO$_4$ and the solvent removed in vacuo. GC analysis on 10% SE-30 on Chromosorb W AW/DMCS showed a large amount of 26, a minor amount of 30, and a small shoulder on the dicyclopentadiene peak which was later indentified as the rearranged hydrocarbon (35). Preparative gas chromatography of the area after 26 and one-fourth up the dicyclopentadiene peak afforded the rearranged product (35), a small amount of the exo-isomer (34), a small amount of the dicyclopentadiene and a large amount of 26. No endo-isomer (29) was seen by NMR. Some rearrangement may have occurred during chromatography. All of the products were identified by comparison of the mixture NMR with those of the pure compounds and by GC/MS.

Preparation of potassium $\tau$-butoxide supported on Chromosorb W. Chromosorb W Non-Acid Washed (45/60 mesh) was dried by heating at 500$^\circ$C for 3 hours with slow nitrogen flow in a tube furnace. A slurry of potassium $\tau$-butoxide (15 g) and the silica gel (31 g) in tetrahydrofuran (250 ml) was refluxed for 1 hour. The solvent was then removed by distillation under nitrogen. The solid was dried under
vacuum overnight.

Methylenecyclopropane (1). The reaction tube (21 cm X 3.5 cm with a 34/45 ground-glass joint at the top and a 14/20 joint at the bottom) was loaded with 6 cm of glass wool, 3 cm of Chromosorb W, 4 cm of potassium tert-butoxide on Chromosorb W, and 2 cm of Chromosorb W. The entire apparatus was placed under vacuum (0.01 mm Hg) and the portion of the tube containing the Chromosorb W was heated to 240°C by means of a heating tape. The temperature was measured by a thermocouple inserted into a small tube placed between the reaction tube and the heating tape. There was a series of four traps, the first two cooled by dry ice/acetone baths and the latter two by liquid N₂ baths. Once the system had equilibrated, the rate of addition of 31 was controlled by cooling the flask containing 31 to ca. -50°C. For the NMR studies, tetrahydrofuran-d₈ was introduced into the first liquid N₂ cooled trap so that the tetrahydrofuran-d₈ froze at the top of the trap. An NMR tube was attached to the bottom of the U-trap. After the reaction, the trap was closed off from the vacuum pump and the liquid N₂ bath replaced with a pentane/liquid N₂ bath cooled to ca. -100°C. After the solution collected in the NMR tube, the tube was sealed. The NMR spectra were then recorded at ca. -100°C. For the IR and mass spectral studies, methylenecyclopropene (1) was collected in the first liquid N₂ cooled U-trap. The trap was then closed off and removed from the apparatus. The trap was then attached to the IBM Model 98 FTIR.
spectrometer, the Finnigan Model 3300 direct inlet mass spectrometer, or the double-focusing CEC 21-110 mass spectrometer. The cold trap was slowly warmed from -120 to -80°C and the spectra recorded. \(^1\)H NMR (tetrahydrofuran-\(d_8\)) \(\delta\) 3.47 (t, \(J=2.2\) Hz), 8.61 (t, \(J=2.2\) Hz); \(^{13}\)C NMR (tetrahydrofuran-\(d_8\)) \(\delta\) 59.57 (t, \(J_{\text{CH}}=161.5\) Hz), 132.90 (t, \(J_{\text{CH}}=228.5\) Hz). Mass spectrum calculated for \(C_4H_4\): m/e 52.0313; found m/e 52.0312.

3-Chloro-3-methyltricyclo[3.2.1.0\(^2,4\)]oct-6-ene (36). \(n\)-Butyl lithium (1.3 M, 110 ml, 0.14 mol) was added dropwise over 45 min to a cooled (-30 to -40°C) solution of norbornadiene (26.4 g, 0.29 mol), 1,1-dichloroethane (14.2 g, 0.14 mol) and ether (50 ml). The mixture was stirred for 30 min before warming to 0°C. Water was then slowly added. The layers were separated and the organics were washed with water (2X), brine (1X), dried over MgSO\(_4\) and the solvent removed in vacuo. The residue was distilled under vacuum (0.5 mm Hg), bath temperature 45-60°C. GC analysis (5% Carbowax 20M on Chromosorb W AW/DMCS) showed 4 peaks, two major ones and two minor ones. The mixture was shown to be isomeric by GC/MS. The mixture was used without further purification. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.6-2.2 (m), 3.0 (s), 6.5 (s). Mass spectrum calculated for \(C_9H_{11}Cl\): m/e 154.0549, 156.0520; found m/e 154.0553, 156.0522.

3-Methylene(1.2.4.5)tricyclo[3.2.1.0\(^2,4\)]oct-6-ene (34). A solution of
the mixture (36) (2.0 g, 13 mmol) in dimethyl sulfoxide (10 ml) was added to a mixture of potassium t-butoxide (7.26 g, 65 mmol) in dimethyl sulfoxide (25 ml). The mixture was stirred for 2 hours, then water was added. The aqueous phase was extracted with pentane (4X) and the combined organics were washed with water (4X), brine (1X), dried over MgSO₄ and the solvent removed in vacuo. A sample for analysis was purified by preparative gas chromatography (10% FFAP on Chromosorb W AW/DMCS). ¹H NMR (CDCl₃) δ 0.91 and 1.14 (AB quartet, 2H, J=8.3 Hz), 1.52 (s, 2H), 3.00 (s, 2H), 5.22 (s, 2H), 6.35 (m, 2H). ¹³C NMR (CDCl₃) δ 27.49, 42.03, 44.27, 102.22, 139.39, 147.78. Mass spectrum calculated for C₉H₁₀: m/e 118.0783; found m/e 118.0782.

Thermalysis of 34. A sample of 34 (20-30 mg) in toluene-d₈ (0.4 ml) was degassed and sealed in an NMR tube. The tube was heated at 145°C for 10 min. NMR analysis indicated 70-80% completion. Analysis after an additional 40 min at 145°C showed complete conversion to 35. ¹H NMR (CDCl₃) δ 1.4-2.3 (m, 8H), 4.87 (s, 2H). ¹³C NMR (CDCl₃) δ 25.88, 26.22, 28.52, 30.86, 103.10, 113.53. Mass spectrum calculated for C₉H₁₀: m/e 118.0783; found m/e 118.0782.
References and Notes


32. I thank Dr. Lewis and his group for the use of their vacuum line.


34. I thank Drs. Robert Hauge, Zakya Kafafi and Judy Chu for assistance in securing the infrared spectrum.

35. I thank Dr. Terry Marriott for the mass spectral studies.
Study of the Dehydrochlorination of Aromatic

gem-Dichlorocyclopropanes and the Synthesis of

1H-Cycloprop[b]anthracene
Attempted Synthesis of 1H-Cyclopropa[b]phenanthrene:

A Study of the Dehydrochlorination of Aromatic gem-Dichlorocyclopropanes
INTRODUCTION

Cyclopropyrenes have long been a fascination to chemists who wish to study the strain, bonding and reactivity of these compounds. A variety of cyclopropyrenes have been synthesized and studied to determine the amount of strain and distortion that can be incorporated in the aromatic framework. The strain energies of some cyclopropyrenes are given in Table I. The preparation of the shock-sensitive 3\(^4\) indicates that the limits of strain may have been reached.

The concept of bond fixation, first formulated by Mills and Nixon, and later reinterpreted by Coulson has been applied to the cyclopropyrenes and the effects of a 1,2-methylene fusion. The X-ray crystallographic data of several cyclopropyrenes are given in Table II. Each compound except 4 exhibits the same pattern, three short bonds in sequence (b, a, b'). Unfortunately, this does not correspond to either Kekule structure, in accordance to bond fixation. The shortened "a" bond may be the result of compression by the bridging methylene.

There are numerous schemes for the synthesis of the various cyclopropyrenes, however, none seems to be universal. The first cyclopropabenzene derivative was synthesized by Anet and Anet via the photolytic elimination of nitrogen from the 3H-indazole (7) (eq. 1). This method is limited to gem-disubstituted cyclopropabenzenes.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Strain Energy (Kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<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>
</tr>
<tr>
<td>Compound</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2</td>
<td>1.368</td>
<td>1.337</td>
</tr>
<tr>
<td>4</td>
<td>1.333</td>
<td>1.385</td>
</tr>
<tr>
<td></td>
<td>(1.389)</td>
<td>(1.412)</td>
</tr>
<tr>
<td>5</td>
<td>1.35</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>(1.42)</td>
<td>(1.38)</td>
</tr>
<tr>
<td>6</td>
<td>1.339</td>
<td>1.355</td>
</tr>
</tbody>
</table>

The numbers in parenthesis denote the b', c' and the e' bond lengths.
A similar route by Dürr and co-workers provided the first cyclopropa[al]naphthalene (9) (eq. 2) and the only spirocyclopropene (10) (eq. 3).

Vogel and his co-workers have developed an elaborate and elegant method for preparing the parent cyclopropabenzene (1) and
cyclopropa[a]naphthalene (11) (eq. 4). The crucial step is a retro Diels-Alder reaction under flash vacuum pyrolysis conditions. The high temperatures involved restrict its use to those compounds of high to moderate thermal stability.

The intramolecular cyclization method of Radlick and Crawford of preparing 1 has been applied to 11 and 12 (eq. 5) albeit in very low yields, 4% and 5% respectively. An attempt by Halton and co-workers to prepare cyclopropa[1]phenanthrene (13) by this method has failed. This is the only reported attempted synthesis of a cyclopropaphenanthrene.
An excellent synthesis of gem-dihalocyclopropenenes involves the double-dehydrohalogenation of the related tetrahalo precursors. This method relies on the Diels-Alder reaction of a tetrahalocyclopropene with the required diene. Several gem-dihalocyclopropenenes have been prepared in this manner. The most recent application has been the synthesis of 1,1-dichloro- (14) and 1,1-difluorocycloprop[b]anthracene (15) by Muller and Rey (Scheme I).\textsuperscript{19,20} This is the first successful synthesis of a cycloprop[b]anthracene derivative.

The double dehydrohalogenation-isomerization of gem-dihalobicyclo-[4.1.0.]heptenes has been very successful in the benzene and naphthalene series.\textsuperscript{21-23} The proposed mechanism for this reaction is a series of elimination-isomerizations reactions (Scheme II). Labeling experiments of Prestien and Gunther\textsuperscript{24} support this mechanism, as a $^{12}_C$ label at C-1 retained its position (eq. 6).

\begin{align*}
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}

(eq. 6)
Scheme I

\[
\text{Scheme II}
\]

14, \( X = Cl \)
15, \( X = F \)
Transient cyclopropenes of type 17 and 19 have been trapped as Diels-Alder adducts\\(^{25}\) (Scheme III) and with nucleophiles, such as methyl mercaptide\\(^{26}\) (Scheme IV). Coburn and Jones\\(^{25}\) trapped the cyclopropene (22), formed from the rearrangement of the dibenzo[a,c]cycloheptatrienyldene (21), with several dienes. Billups and co-workers\\(^{26}\) trapped the cyclopropene (26) formed by the dehydrochlorination of 25 with methyl mercaptide. The bicycloheptatrienes are sufficiently long-lived to experience trapping with dienes or nucleophiles but in the absence of trapping agents, readily rearrange to give the arylcarbenes. Addition of nucleophiles to cyclopropenes is well documented.\\(^{26-29}\) As such, the transient cyclopropenes formed in the double dehydrohalogenation-isomerization reactions should be readily trapped and the mechanism supported.
Scheme III

\[ \text{N=N-SO}_2\text{Ar} \rightarrow \text{21} \]

\[ \text{20} \rightarrow \text{22}, \; X = \text{CH}_2 \]

\[ \text{23}, \; X = \text{CH}_2 \]

\[ \text{24}, \; X = 0 \]
Scheme IV

25 \xrightarrow{\text{t-BuOK}} 26

\xrightarrow{\text{MeSK}} 27
RESULTS AND DISCUSSION

Although cycloprop[b]anthracene \(28\) proved impossible to prepare via the double dehydrohalogenation-isomerization route,\(^{30,31}\) its structural isomer, cycloprop[a][b]phenanthracene \(29\) appeared attractive. The prevailing theory for the apparent instability of \(28\) has been a greater degree of bond localizations and the negative effects of the dimethylenecyclopropane resonance structures of \(28\) (i.e. \(28a, b, c\)).\(^{30,31}\) However, cycloprop[a][b]phenanthrene possesses a stable "cycloprop[a][b]naphthalene" moiety. Further, resonance structure \(29a\) possesses three "good" benzene rings which should impart greater stability on \(29\). There also exists an 8 Kcal/mol resonance energy difference from anthracene (84 Kcal/mol) to phenanthrene (92 Kcal/mol) which should stabilize \(29\) relative to \(28\).
The needed precursor for 29 was the dichloride 31, formed from the addition of dichlorocarbene to 1,4-dihydrophenanthrene (30). A critical step in this sequence (Scheme V) was the preparation of 30.

Scheme V

Metal-ammonia reductions of phenanthracene yield only 9,10-dihydrophenanthracene (32).\(^{32}\) Compound 30 has been prepared in low yield (6.6%) as a mixture of 30 and 32 (1 to 10 ratio) in the lithium/tetrahydrofuran reduction of phenanthrene.\(^{33}\) The route taken here was the photocyclization of \(\varepsilon\)-stilbene in \(\varepsilon\)-propyl amine as reported by Buquet, Couture and Lablache-Combier.\(^{34}\) Although a mixture was formed, 30 was reported in 70% yield. However, in our hands the
yield was approximated at 30%. No attempt was made to purify since the impurities would not interfere in the subsequent reaction. The photolysis was carried out in degassed 1-propyl amine under N₂ at 2537Å for 64 hours. Chromatography on silica gel (benzene, hexane) afforded 450 mg (45% yield) of a 70:30 mixture (NMR) of 30 to 32 and 1,2-diphenylethane.

Addition of dichlorocarbene (potassium t-butoxide, CHCl₃, pentane) afforded 31 in ca. 30% yield. Recycling the mixture twice completely consumed 30. Purification of 31 was accomplished by column chromatography on silica gel (benzene, hexane) and recrystallization from CH₂Cl₂, m.p. 120-122°C.

Reaction of 31 with potassium t-butoxide in tetrahydrofuran at 0°C for 1.5 hours afforded 2- and 3-chloromethylphenanthrene (33) in 70% yield (eq. 7) after chromatography on silica gel (hexane). The ratio of one isomer to the other was 1 to 3.5 (NMR). Attempts to trap the expected cyclopropenes (35a, b) with methyl mercaptide in dimethyl sulfoxide afforded a quantitative yield of the isomeric 2- and 3-(thiomethyl)methylphenanthrenes (34) in a ratio of 1 to 2.75 (NMR). As none of the cyclopropenes were trapped, it appeared that the cyclopropenyl double bond, if indeed formed, rapidly isomerized out of the ring.
$\text{Cl} \quad \text{Cl} \quad \rightarrow \quad \text{CH}_2X$

(eq. 7)

$33, X = \text{Cl}$

$34, X = \text{SMe}$

$35a$

$35b$
An attempt was then made to trap the expected transient cyclopropanes in the attempted synthesis of 1H-cycloprop[b]anthracene (28). In the absence of methyl mercaptide nucleophile, elimination of dichloride (36) yielded only 2-chloromethylnaphthalene (37) and the corresponding t-butyl ether (38) (eq. 8).\textsuperscript{30,31}

\begin{center}
\begin{tikzpicture}
\node[above] at (0,0) {\textcircled{36}};
\node[above] at (2,0) {\textcircled{37}, X = Cl};
\node[above] at (2,-0.5) {\textcircled{38}, X = O-t-Bu};
\node at (1.1,-2.5) {\textcircled{(eq. 8)}};
\draw[->] (0,0) -- (2,0);
\end{tikzpicture}
\end{center}

Reaction of 36 in the presence of methyl mercaptide in dimethyl sulfoxide afforded only the 2-(thiomethyl)methylnaphthalene (39) in 94\% yield (eq. 9). Purification by preparative thin layer chromatography (silica gel, hexane) afforded 39 as a yellow solid, m.p. 115-118°C.

\begin{center}
\begin{tikzpicture}
\node[above] at (0,0) {\textcircled{36}};
\node[above] at (2,0) {\textcircled{39}};
\node at (1.1,-2.5) {\textcircled{(eq. 9)}};
\draw[->] (0,0) -- (2,0);
\end{tikzpicture}
\end{center}

Again, the expected transient cyclopropanes were not trapped, indicating that (1) the reaction proceeded through a different
mechanism, or (2) the methyl mercaptide was not a strong enough nucleophile, that is, the elimination-isomerization was too facile.

The elimination of the cyclopropa[b]naphthalene precursor (40) has generated considerable controversy.\textsuperscript{35-38} It well established that 40 gives 2 when treated with potassium t-butoxide in tetrahydrofuran, however the yields are exceedingly low when the solvent is dimethyl sulfoxide.\textsuperscript{37} This appears significant since the reverse is true for the synthesis of 1. Also, unusual products arising from skeletal rearrangements have been isolated by Halton and co-workers\textsuperscript{35,36} but not by those in this laboratory.\textsuperscript{37,38} It was hoped that this study would clarify the situation. In this laboratory, only three products were seen 2, 41, and 42 in the elimination of 40 (eq. 10).\textsuperscript{37,38} It has been demonstrated that 2 solvolyzes very slowly to 42 and that the majority of 42 seen must then come from 41.\textsuperscript{36} Initial work by Halton using varying base concentrations afforded three products of varying
proportions (eq. 11).\textsuperscript{35}

The unusual product 43 was later re-identified as 44 in a later publication.\textsuperscript{36} Also in that paper, 42 was re-identified as 45, stating that 42 was seen only as a slight impurity (ca. 1%). The proposed mechanism for this extensive skeletal rearrangement involved an unprecedented $S_N^2$ attack on a gem-dichlorocyclopropane (Scheme VI).\textsuperscript{35,36}
Scheme VI

40

44

45
In the methyl mercaptide trapping study, it was found that the methyl mercaptide, not rigorously purified, could contain impurities which lead to these unusual products. The addition of dichlorocarbene to 1,4-dihyronaphthalene (46) can lead to two impurities (eq. 12). One impurity is the isomeric 47 which would arise from 1,2-dihyronaphthalene impurities in 46. This compound was later identified (GC, GC/MS) in the impure 40 initially used in this study. The other, 1-(dichloromethyl)-1,4-dihyronaphthalene (48), is formed from the insertion of dichlorocarbene into the benzyl-allylic C-H bond. This compound was not identified in the impure 40, however, its presence is inferred from the products isolated from the methyl mercaptide trapping.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{C} & \quad \text{CHCl}_2
\end{align*}
\]

(eq. 12)

Insertion reactions of singlet carbene (\(\text{CH}_2\)) into C-H bonds of alkanes is well documented. The first insertion of dichlorocarbene into C-H bonds was in 1961 by Parham and Koncos. They reported the apparent insertion of dichlorocarbene into the C-H bonds of 2H-1-benzothiopyrone (49) (Scheme VII).
The two insertion products 50 and 51 were obtained in a 2.4 : 1 ratio when the dichlorocarbene was generated from ethyl trichloroacetate and sodium methoxide and in a 1 : 1 ratio when generated from the thermal decomposition of sodium trichloroacetate. No dichlorocyclopropane adduct (52) was observed. The reaction presumably proceeds via the ambidient ion 53.
However, when 4H-1-benzothiopyrone (54) was reacted under the same conditions, only the "normal" cyclopropane adduct (55) was formed (eq. 13). This would suggest that the reactions do not proceed through a common intermediate (e.g. 53) and that the sulfur atom has an important effect on the course of the reaction.

![Chemical Structure]  

(eq. 13)

Fields, in 1962, reported\textsuperscript{41} the first insertion products of dichlorocarbene into the C-H bonds of alkyl-substituted aromatics (analogous to the system studied here). Five compounds were studied: cumene (56), ethyl benzene, p-diisopropyl benzene, tetralin, and diphenylmethane. Each reacted with dichlorocarbene to yield a C-H bond insertion product of type 57 (eq. 14).
The highest yields were obtained when the dichlorocarbene was generated by the thermal decomposition of sodium trichloroacetate (17-39%). If the dichlorocarbene was generated from ethyl trichloroacetate and sodium methoxide or chloroform and potassium the yields decreased to 5 and 0.5% respectively. It is interesting to note that Halton and co-workers\textsuperscript{35,36} employed the second method and those in the Billups laboratory\textsuperscript{37,38} used the latter method.

1-(Dichloromethyl)-1,4-dihydronaphthalene (48) under the reaction conditions will lead to the substituted 1-methylnaphthalenes, compounds 44, 45, 58 (Scheme VIII).

Reaction of rigorously pure 40 (pure by NMR, TLC, GC/MS) afforded 59 as the major product and 60 and 61 (ca. 6\% combined yield) as minor impurities (eq. 15). Compounds 60 and 61 were tentatively identified by their spectral properties. No 1-(thiomethyl)methylnaphthalene (58) was seen. When impure 40 was used, two new products were observed, 62 and 58.
Scheme VIII

48 \[ \text{H} \quad \text{CHCl} \]

\[ \quad \rightarrow \quad \]

\[ \text{Cl} \quad \circ \quad \text{H} \]

\[ \quad \rightarrow \quad \]

\[ \text{CH}_2X \]

44 \[ \text{CH}_2\text{Cl} \]

\[ \quad \rightarrow \quad \]

\[ \text{CH}_2X \]

45, \( X = \text{o-\tau-Bu} \)

58, \( X = \text{SMe} \)
Compound 62 was found to come from 47 (described below) a known impurity in the initially used 40. Compound 58 may arise from 1-(dichloromethyl)-1,4-dihydronaphthalene (48) the other probable impurity of 40. As the unusual products can be accounted for by reasonable impurities (i.e., they are not formed when rigorously pure starting materials were used) a mechanism involving an $S_N2$ attack on a gem-dichlorocyclopropane does not have to be invoked.

As noted above, the elimination of 47 has been investigated by Halton and co-workers$^{42}$ and by members of this laboratory.$^{38,43}$ Halton
saw three products in the elimination (potassium $\varepsilon$-butoxide, tetrahydrofuran) of 47. Compounds 44, 45, and 63 were isolated in yields of 9%, 8%, and 12% respectively (eq. 16).

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
47 & \quad \rightarrow \\
\text{CH}_2\text{Cl} & \\
44 & \\
\text{(eq. 16)} & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{O-}$\varepsilon$-Bu & \quad \text{Cl} & \quad \text{H} & \quad \text{O-}$\varepsilon$-Bu \\
45 & \quad \text{+} & \quad 63 & \quad \text{+} & \quad 64 \\
\end{align*}
\]

In this laboratory, 44 was not seen, however, 45, 63, and 64 were isolated in yields of 26%, 9%, and 4% respectively (eq. 16). The elimination of 47 in the presence of a low concentration of methyl mercaptide nucleophile afforded 65. In the presence of a high concentration, only 62 was isolated (eq. 17). In the trapping experiment, no 58 was seen by NMR ($^1$H and $^{13}$C).
Since the dehydrochlorination-isomerization of the cyclopropabenzene precursor (16) was the only reaction to proceed readily in dimethyl sulfoxide, the elimination-trapping study of 16 in dimethyl sulfoxide provided the best results. Elimination of 16 in dimethyl sulfoxide in the presence of methyl mercaptide afforded six products (eq. 18), three of which were trapped cyclopropenes. These three products were readily separated by preparative gas chromatography and the other three remained a mixture. The ratio of the products was dependent on the reaction time (Table III). The products were identified as follows: 1-thiomethyl-7-chlorobicyclo[4.1.0]hept-3-ene (66), 1,7-(bisthiomethyl)bicyclo[4.1.0]hept-3-ene (67), 1-thiomethyl-6-methylenebicyclo[3.1.0]hex-2-ene (68), o-thiomethylmethylbenzene (69), 2-thiomethyltoluene (70), and 1-thiomethylcyclohepta-2,4,6-triene (71). The stereochemistry of 66 was determined by the large coupling constant (J=8 Hz) of cis-cyclopropyl hydrogens and the observed syn addition of nucleophiles to cyclopropenyl double bonds. Compound 67 was
similarly identified by its small coupling constant (J=1.8 Hz) and two syn additions. Compound 68 arose from a methylenecyclopropane rearrangement (Scheme IX). The stereochemistry was determined by NMR. Compound 72 was rejected since the lone cyclopropyl hydrogen appeared as a triplet and are not coupled to the olefinic protons. The $^{13}$C NMR spectrum was also consistent with this structure.
Table III

Product Distribution Ratios as a function of time for eq. 18.

<table>
<thead>
<tr>
<th></th>
<th>66</th>
<th>67</th>
<th>68</th>
<th>69, 70, 71</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>42.2%</td>
<td>17%</td>
<td>8.9%</td>
<td>32%</td>
</tr>
<tr>
<td>2.5 hours</td>
<td>4.8%</td>
<td>31.1%</td>
<td>11.9%</td>
<td>52.1%</td>
</tr>
</tbody>
</table>

As determined by gas chromatography, the average of several gas chromatograms was taken.
The three compound mixture was subjected to gas and thin layer chromatography without success. All three compounds exhibit a molecular ion of m/e 188. Compound 69 was identified by comparison of its spectral data ($^1$H and $^{13}$C NMR) with an authentic sample prepared from benzyl chloride and methyl mercaptide. Compound 70 was similarly identified by comparison with a sample of 2-thiomethyltoluene prepared from o-methylthiocresol. The structure of 71 was assigned based on its spectral data and from the probable products expected from the proposed mechanism. The $^1$H NMR spectrum showed a doublet (1 H) at $\delta$ 2.6 (J=6.8 Hz) coupled to an olefinic proton. The olefinic multiplet collapsed to a doublet when irradiated at 2.6 ppm.
Two previously studied systems were also investigated, and new results were obtained. In the elimination-trapping reactions of 7,7-dichloronorcarane (73) by Shields and Gardner, only cis-7-chloro-1-thiomethylbicyclo[4.1.0]heptane (74) was isolated in 69% yield after distillation. No disulfide was reported. This was not surprising since the ratio of the reactants (62:potassium tert-butoxide:methyl mercaptide) was 1:2.7:1.27. In this study the ratio was 1:12:5 and both products were observed, 74 and 1,2-bis(thiomethyl)bicyclo[4.1.0]heptane (75) (eq. 19), in a ratio of 36:64. When the ratio of reactants was reduced, the product ratio was 35:48 with 17% unreacted 73. The stereochemistry of 75 was determined by NMR (1H and 13C). The 13C NMR spectrum showed only five peaks indicating a symmetrical molecule. The reason for the different stereochemistry in 67 and 75 are unknown. However, this was also seen in the following case.

The elimination-trapping of 7,7-dichlorodibenzo[a,c]bicyclo[4.1.0]heptane (76) has been reported to give only one product, 1,2-bis(thiomethyl)dibenzo[a,c]bicyclo[4.1.0]heptane (77). In this study, this product was seen in addition to 1,7-bis(thiomethyl)dibenzo-
[a,c]bicyclo[4.1.0]heptane (78) in a ratio of 3 to 1 (eq. 20). Compound 77 was identical to the previously reported compound.\(^\text{26}\) Compound 78 was identified on the basis of its NMR spectra (\(^1\)H and \(^{13}\)C). The two thiomethyl groups appeared at \(\delta 2.25\) and 2.06 as opposed to \(\delta 2.13\) for 77. The cyclopropyl hydrogens appeared as a pair of doublets (\(J=5.3\) Hz) at \(\delta 2.88\) and 1.88 as opposed to \(\delta 1.82\) and 0.76 (\(J=5.5\) Hz) for 77.

\[ \text{76} \quad \text{77} \quad \text{78} \]

The \(^{13}\)C NMR spectra clearly show that 77 was a symmetrical molecule while 78 was an unsymmetrical molecule. Compound 77 displayed the bridging methylene carbon as a triplet at \(\delta 26.32\). Compound 78 displayed two cyclopropyl carbons as doublets at \(\delta 38.42\) and 40.18.

These two results demonstrate that methyl mercaptide is an effective trapping agent for cyclopropenes which do not rapidly isomerize.

The results of this study indicate that two mechanisms are involved in the elimination of gem-dichlorocyclopropanes. The first mechanism (Scheme II) is a sequence of two elimination-isomerization reactions which lead to the appropriate cyclopropaprene. The second
involves an elimination-isomerization followed by abstraction of the benzylic (allylic) proton, aromatization and ring opening (Scheme X).

Scheme X

\[
\begin{array}{c}
\text{R = benzo} \\
\end{array}
\]

This second mechanism accounts for the failure to form the higher cyclopropenes by this method. It evidently becomes more important in the higher analogs and may be solvent and/or base dependent as the reaction of 16 and 40 are strongly dependent on solvent and base concentration.

Another important aspect of this study is that it demonstrated the need to place the leaving groups at the bridgehead instead of out on the three-membered ring. The success of this method is seen in the 1,1-dihalocyclopropenes which have been prepared by the elimination of bridgehead halogens. There are two approaches to this problem. The first is to add dichloro carbene to the appropriate 1,2-dihaloalkene. This approach was attempted by Muller and Rey\textsuperscript{20} in the attempted
synthesis of 1,1-dichloro-1H-cycloprop[b]anthracene (14) (eq. 21). However, repeated attempts to add the carbene by the conventional methods failed.

The second involves a Diels-Alder of a 1,2-dihalocyclopropene to the appropriate diene. This method relies on the reduction of tetrachlorocyclopropene (79) with tri-n-butyltin hydride. The useful 1,2-dichlorocyclopropene (80) is prepared in low yield in a mixture with the 1,3- and 3,3-dichlorocyclopropenes (81, 82) (eq. 22).47

A new synthetic sequence for the preparation of 1,2-dihalocyclopropenes has recently been developed in this laboratory.
and has been applied to the synthesis of 1H-cycloprop[b]anthracene, the first parent homolog of cyclopropabenzenene and cyclopropa[b]naphthalene to be prepared in ten years. The results of this work is described in the following section.
Synthesis of 1H-Cycloprop[b]anthracene
Work described in the previous section indicated that the dehydrohalogenation-isomerization of 1,1-dihalobicyclo[4.1.0]hept-3-enes was incompatible with the higher analogs. It was obvious that the ideal precursor to the higher analogs would be of type 83 where the leaving groups are positioned at the bridgehead carbons.

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

\[R = \text{benzo}\]

83

However, a synthetic sequence to such precursors was lacking until the recent synthesis of 1-bromo-2-chlorocyclopropene (84) in this laboratory.\(^{48}\) A pathway similar to that of Muller and Rey\(^{19,20}\) was utilized in the synthesis of 1H-cycloprop[b]anthracene (28).

The required diene, 2,3-dimethylene-1,2,3,4-tetrahydronaphthalene (85), has been prepared by a number of methods.\(^{19,20,49}\) Compound 85 was prepared by the pyrolysis of 1,4-dihydrocyclobuta[b]naphthalene (86) (Scheme XI).\(^{49}\) 1,2-Dimethylenecyclobutane (87)\(^{50}\) was readily available from the thermal dimerization of allene.\(^{51}\)
The dihalocyclopropene (84) was prepared via the fluoride elimination\textsuperscript{52} of 88 (eq. 23). After the preparation of 84, the tetrahydrofuran solution was vacuum distilled into a liquid N\textsubscript{2} cooled trap containing the diene (85). The reaction mixture (Scheme XII)
was stirred at \(-20^\circ\text{C}\) for several hours, then stored at \(-20^\circ\text{C}\) overnight. After stirring for several more hours at \(-20^\circ\text{C}\), the mixture was allowed to warm to room temperature. The cyclopropene (84) was found to be stable at \(-20^\circ\text{C}\) for days and at room temperature for several hours. However, 84 had completely decomposed after 30 hours at room temperature. Compound 89 was isolated in 76\% yield. Purification was accomplished by column chromatography on silica gel (benzene, hexane) and recrystallization from pentane, m.p. 147-148\(^\circ\text{C}\). Compound 89 was oxidized to 90 upon treatment with DDQ in CCl\(_4\) at 25\(^\circ\text{C}\) for 20 hours.
Initial chromatography on silica gel (CH₂Cl₂) afforded a yellow solid which was purified by column chromatography on silica gel (benzene, hexane) and recrystallization from n-pentane to yield white needles, m.p. 140-141°C in 64% yield. Conversion to 28 was effected by treatment of 10 with potassium n-butoxide in tetrahydrofuran at -78°C. After warming to -30°C, the solvent was removed in vacuo and the residue extracted with n-pentane (2X) to yield nearly pure 28 in 41.5% yield.

The ¹H NMR spectrum of 28 displays the expected anthracene pattern with singlets at δ 3.56 (bridging -CH₂), 7.67 (H₂, H₉) and 8.41 (H₃, H₈) and an AA'BB' system at δ 7.34-7.60 (H₅, H₆) and 7.86-8.12 (H₄, H₇). The ¹³C NMR spectrum shows signals at δ 18.6 (C1), 111.6 (C2, C9), 123.3 (C1a, C9a), 125.3 (C5, C6), 126.6 (C4, C7), 128.1 (C3, C8), 131.7 (C3a, C7a), and 135.2 (C2a, C8a). These assignments were based on comparison with similar systems. The ultraviolet spectrum (n-hexane) exhibits a maximum at 252 nm (ε 117,000) with other absorptions at 320 (ε 1500), 334 (ε 3500), 351 (ε 5300), and 371 (ε 4700). The infrared spectrum showed the characteristic benzene "double bond" at 1678 cm⁻¹. Elemental composition was provided by high resolution mass spectrometry; calculated for C₁₅H₁₀: m/e 190.0783, found 190.0781.

The ease of synthesis of 28, its apparent stability, and the lack of unusual spectral properties indicate that the failure to form 28 by the dehydrohalogenation-isomerization route stems not from any greater degree of bond localization but from the failure of the method itself.
X-ray crystallographic analysis to determine exact bond lengths is awaiting the preparation of larger quantities of 28.

Two other annelated cyclopropaarenes were also prepared from Diel-Alder adducts of 84. Treatment of 89 with potassium t-butoxide in tetrahydrofuran at $-78^\circ$C followed by the same work-up yielded a nearly quantitative conversion to a 77:23 mixture (NMR) of 3,8-dihydro-1H-cycloprop[bl]anthracene (91) and 2-methylanthracene (92), respectively (eq. 24).

![Chemical structure](image)

Compound 91 was identified by its $^1$H NMR spectrum, exhibiting singlets at $\delta$ 3.27 (bridging $-\text{CH}_2$) and 3.95 ($H_3$, $H_8$) and aromatic signals extending from ca. 7.0 to 7.5. Compound 91 decomposed at $-20^\circ$C after ca. 36 hours. It is interesting to note that a previous attempt by Garratt$^{30}$ to prepare this compound from the gem-dihalocyclopropane (93)
yielded only 2-methylantracene (92) (eq. 25).

\[
\begin{align*}
\text{C1} & \quad \text{C1} \\
& \quad \text{DMSO} \\
& \quad \text{t-BuOK} \\
\end{align*}
\]

The third cyclopropa[\(\alpha\)]phenanthrene (94), the first reported cyclopropaphenanthrene derivative. The required diene, 1-vinyl-3,4-dihydronaphthene (95),\(^{56}\) was prepared as outlined in Scheme XIII.

Scheme XIII

\[
\begin{align*}
\text{Br} & \quad \text{Mg} \\
\text{THF} & \quad \text{HO} \\
\end{align*}
\]

\[
\begin{align*}
\text{I}_2, 100^\circ C & \quad \text{toluene} \\
\end{align*}
\]
The addition of vinyl grignard to α-tetralone afforded the alcohol (96) in 88% distilled yield, b.p. 84-86°C/0.1 mm Hg. Dehydration was accomplished by heating a toluene solution of the alcohol to 100°C for 1 hour with 5 mol% iodine. Purification afforded a 64% yield of diene 95. The reaction of 95 with cyclopropene 84 as described earlier afforded 97 in 85% yield. The stereochemistry of 97 is uncertain. The other isomer is equally likely. Purification by column chromatography on silica gel (benzene, hexane) and recrystallization from pentane afforded 97 as a white solid. Treatment of 97 (Scheme XIV) with potassium tert-butoxide in tetrahydrofuran at

Scheme XIV

\[
\begin{align*}
\text{95} & \quad + \quad \begin{array}{c}
\text{Br} \\
\text{Cl}
\end{array} \\
\text{84} & \quad \xrightarrow{\text{THF}} \quad \begin{array}{c}
\text{Br} \\
\text{Cl}
\end{array} \\
\text{97} & \quad \xrightarrow{\text{t-BuOK}} \quad \begin{array}{c}
\text{94}
\end{array}
\end{align*}
\]
-78°C to -10°C followed by solvent removal and residue extraction afforded 94 in 85% yield. The $^1$H NMR spectrum of 94 exhibited singlets at $\delta$ 2.90 (H$_2$H$_3$)$_{58}$ and 3.26 (bridging -CH$_2$) and aromatic multiplets at $\delta$ 7.12-7.40 (4H) and 7.56-7.80 (2H). An attempt to aromatize 94 using DDQ yielded uncharacterized products.

This route has proven the value of 84 in the synthesis of heretofor inaccessible cyclopropenes. And it promises to be invaluable in the synthesis of the higher homologs and other strained ring systems, which may provide insight into the limits of strain and distortion which can be imposed on an aromatic system.
EXPERIMENTAL

General. Proton magnetic resonance spectra were recorded using a Varian Model EM-390 (90 MHz) or a JEOL FX90Q (90 MHz) spectrometer. $^{13}$C NMR spectra were recorded on a JEOL FX90Q (22.63 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from TMS. Unless otherwise noted, NMR spectral data were obtained as a chloroform-d$_1$ solution. Infrared spectra were recorded on a Beckman IR 4230 spectrometer as solutions in carbon tetrachloride and carbon disulfide. Ultraviolet spectra were recorded in hexane solution on a Cary 17 spectrometer. High resolution mass spectra were recorded on a double-focusing CEC 21-l10 mass spectrometer, and low resolution mass spectra were recorded on a Finnigan Model 3300 gas chromatograph/mass spectrometer operated at 30 ev. A Hewlett Packard Model 700 gas chromatograph with a thermal conductivity detector and operated at a flow rate of 60 cc of helium per minute was used for all analytical and preparative gas chromatography. All melting points and boiling points are uncorrected.

Tetrahydrofuran was distilled from sodium-benzophenone ketal prior to use. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure prior to use. Column chromatography was performed on Baker reagent grade silica gel (60-200 mesh). Merck precoated silica gel plates were used for analytical (100 X 50 X 0.25 mm) and preparative (200 X 200 X 2 mm) thin layer chromatography. All other chemicals were of reagent quality and used as obtained from the
manufacturers. All reactions were carried out in an inert atmosphere (dry nitrogen) where necessary.

**1,4-Dihydophenanthrene (30)**. Compound 30 was synthesized using the procedure of Buquet, Couture, and Lablache-Combier. A solution of t-stilbene (1.0 g, 5.55 mmol, $1.85 \times 10^{-2} \text{M}$) in $n$-propyl amine (300 ml) was degassed by passing dry nitrogen through the solution for 2 hours. The solution was then irradiated for ca. 64 hours at 2537 Å using three ultraviolet lamps. Periodic aliquots were analyzed by NMR to ensure complete conversion. Removal of the solvent under reduced pressure afforded a yellow oil. The oil was taken up in $\text{CH}_2\text{Cl}_2$, dried over $\text{MgSO}_4$, and the solvent removed in vacuo. The oil was partially purified by column chromatography on silica gel (benzene, hexane), affording ca. 450 mg of a white solid. NMR analysis showed a mixture of $\sim$ and $\sim$ and/or 1,2-diphenylethane (70:30) which was used without further purification or characterization.

**1,1-Dichloro-1a,3a,9a-tetrahydro-1H-cyclopropa[b]phenanthrene (31)**. A slurry of compound 30 (400 mg, 2.22 mmol, 70% pure) and potassium t-butoxide (0.50 g, 4.4 mmol) in pentane (7 ml) was stirred at 0-5°C. Chloroform (0.53 g, 4.4 mmol) was added dropwise via syringe and the mixture stirred for 30 min. Water was added, the layers were separated and the aqueous layer extracted with $\text{CHCl}_3$ (2X). The combined organics were washed with water (1X), brine (1X), dried over $\text{MgSO}_4$ and the
solvent removed in vacuo. This procedure was repeated twice more, until 
~30 was completely converted. Compound 31 was recrystallized from 
CH₂Cl₂, m.p. 120-122°C. ¹H NMR (CDCl₃) δ 1.96-2.4 (m, 2H), 1.9-2.8 
(m, 4H), 7.1-8.1 (m, 6H). Mass spectrum calculated for C₁₅H₁₂Cl₂: m/e 
262.0316, 264.0287; found m/e 262.0309, 264.0287.

2- and 3-Chloromethylphenanthrene (33). A solution of the dichloride 
(31) (110 mg, 0.42 mmol) in tetrahydrofuran (1 ml) was added via 
syringe to a stirred slurry of potassium t-butoxide (375 mg, 3.34 mmol) 
in tetrahydrofuran (5 ml) at 0°C. After 1.5 hours at 0°C, water was 
added and the aqueous layer extracted with pentane (3X). The combined 
organics were washed with water (1X), brine (1X), dried over MgSO₄ and 
the solvent removed in vacuo, affording 104 mg of crude product. 
Purification was accomplished by column chromatography on silica gel 
(hexane) affording 66 mg (70% yield) 2- and 3-chloromethylphenanthrene. 
¹H NMR (CDCl₃) δ 4.65 and 4.70 (s, 2H, ratio 1 to 3.5), 7.37-7.87 (m, 
7H), 8.40-8.63 (m, 2H). Mass spectrum calculated for C₁₅H₁₁Cl: m/e 
226.0549, 228.0520; found m/e 226.0545, 228.0516.

General procedure for the reaction of the dichlorides with potassium 
t-butoxide and methanethiol in dimethyl sulfoxide. Methanethiol (5 eq, 
previously condensed) was distilled under N₂ into a solution of 
potassium t-butoxide (12 eq) in dimethyl sulfoxide. A solution of the 
dichloride (1 eq) in dimethyl sulfoxide was then added dropwise and the
resulting mixture stirred at 25°C for 1-3 hours. Water was then added and the aqueous layer extracted with ether (4X). The combined organics were washed with water (4X), brine (1X), dried over MgSO₄, and concentrated in vacuo.

2- and 3-(Thiomethyl)methylphenanthrene (34). The general procedure was used. The dichloride (31) (117 mg, 0.44 mmol) in dimethyl sulfoxide (3 ml) was added to a stirred solution of methanethiol (0.11 g, 2.22 mmol) and potassium t-butoxide (0.60 g, 5.33 mmol) in dimethyl sulfoxide (10 ml). The resulting mixture was stirred for 2 hours. Work up afforded 107 mg (100% yield) crude product.¹H NMR (CDCl₃) δ 1.88 (s, 3H), 3.71 and 3.78 (s, 2H, ratio 1 to 2.75), 7.30-7.83 (m, 7H), 8.36-8.66 (m, 2H). Mass spectrum calculated for C₁₆H₁₄S: m/e 238.0816, 240.0806; found m/e 238.0815, 240.0807.

2-(Thiomethyl)methylantracene (39). The general procedure was used. The dichloride (36) (0.25 g, 0.95 mmol) in dimethyl sulfoxide (7 ml) was added to a stirred solution of methanethiol (0.23 g, 4.75 mmol) and potassium t-butoxide (1.28 g, 11.4 mmol) in dimethyl sulfoxide (20 ml). The resulting mixture was stirred for 2 hours. Work up afforded 213 mg (94% yield) crude product which was purified by preparative thin layer chromatography (hexane) yielding 39 as a yellow solid, m.p. 115-116°C.¹H NMR (CDCl₃) δ 2.01 (s, 3H), 3.85 (s, 2H), 7.27-7.47 (m, 3H), 7.60-7.73 (m, 3H), 8.17-8.30 (m, 2H). Mass spectrum calculated
for $C_{16}H_{14}$: m/e 238.0816, 240.0806; found m/e 238.0815, 240.0807.

Reactions of pure 1,1-dichloro-1a,2,9,9a-tetrahydro-1H-cycloprop[b]-naphthalene (40) with potassium t-butoxide and methanethiol in dimethyl sulfoxide. The general procedure was used. Compound 40 (1.0 g, 4.7 mmol) in dimethyl sulfoxide (20 mL) was added to a stirred solution of potassium t-butoxide (6.32 g, 56.3 mmol) and methanethiol (1.13 g, 23.5 mmol) in dimethyl sulfoxide (50 mL) for 1.25 hours. Work up afforded 888 mg (quantitative yield based on 59) of crude product. NMR analysis indicated one product, 59, comprising ca. 95% of the mixture. No 1-(thiomethyl)methylnaphthalene (58) was seen by NMR. Preparative thin layer chromatography (hexane, CHCl$_3$/ 5:1) afforded pure 59 and a mixture of isomers (m/e 188) comprising ca. 6% of the total yield. Compounds 58 and 59 were compared to authentic samples. Compound 60 was tentatively identified by its NMR spectrum. Compound 60 displayed a doublet at $\delta$ 3.0 (J=6.5 Hz) which was coupled to an olefinic proton. A series of olefinic protons ranging from $\delta$ 5.6-6.5 were also seen. The methyl group appeared at $\delta$ 2.31. Compound 61 was also tentatively identified by its NMR spectrum. The position of the two methyl groups at $\delta$ 2.56 and 2.47 correlate to those in 70.

Reactions of impure 40 with potassium t-butoxide and methanethiol in dimethyl sulfoxide. The general procedure was used. Impure 40 was treated as above, yielding 1.01 g (from 1.13 g of 40) crude products.
The products were isolated by preparative thin layer chromatography (hexane, CHCl₃/ 3:1) in the following yields: 59 (ca. 70%), 58 (ca. 10%), 62 (6.8%) and 60 and 61 (ca. 5%).

**Reaction of 47 with potassium t-butoxide and methanethiol in dimethyl sulfoxide.** The general procedure was used. The dichloride (47), (34.7 mg, 0.16 mmol) in dimethyl sulfoxide (2 ml) was added to a solution of methanethiol (39 mg, 0.81 mmol) and potassium t-butoxide (219 mg, 1.95 mmol) in dimethyl sulfoxide (2 ml). Work up afforded 36.7 mg (95% yield) crude 62 which was pure by NMR and TLC. ¹H NMR (CDCl₃) δ 1.42 and 1.67 (AB quartet, J=5.4 Hz, 2H), 2.12 (s, 3H), 2.29 (s, 3H), 2.0-2.8 (m, 4H), 6.96-7.36 (m, 3H), 7.96-8.14 (m, 1H); ¹³C NMR (CDCl₃) δ 14.62, 15.93, 27.93, 28.18, 29.28, 40.42, 125.93, 126.76, 128.47, 129.00. Mass spectrum calculated for C₁₃H₁₆S₂: m/e 236.0693, 238.0651; found m/e 236.0696, 238.0653.

**Reaction of 7,7-dichlorobicyclo[4.1.0]hept-3-ene (16) with potassium t-butoxide and methanethiol in dimethyl sulfoxide for 2 hours.** The general procedure was used. The dichloride (16) (0.5 g, 3.1 mmol) in dimethyl sulfoxide (10 ml) was added to a solution of methanethiol (0.74 g, 15.3 mmol) and potassium t-butoxide (4.13 g, 36.8 mmol) in dimethyl sulfoxide (35 ml). The mixture was stirred for 2 hours. Work up afforded 0.49 g crude product. Purification was accomplished by preparative gas chromatography (10% OV-17 on Chromosorb W AW). The
ratio of the products were: 66 (4.8%), 67 (31.1%), 68 (11.9%), and the three component mixture 69, 70 and 71 (52.1%). Two components of the three component mixture were identified by comparison of the spectra ($^1\text{H}$ and $^{13}\text{C}$ NMR) of authentic samples to the spectrum of the mixture. Compounds 69 and 70 were identified in this manner. The spectral data of the pure compounds are listed here. Compound 71 was tentatively identified from the remaining peaks and a knowledge of the probable mechanism. Compound 66: $^1\text{H}$ NMR (CDCl$_3$) δ 1.42-1.66 (m, 1H), 1.9-2.76 (m, 4H), 3.4 (d, J=7.9 Hz, 1H), 5.56 (s, 2H). $^{13}\text{C}$ NMR (CDCl$_3$) δ 13.45, 20.42, 22.18, 27.83, 45.25, 123.29, 123.64. Mass spectrum calculated for C$_8$H$_{11}$Cl$_8$: m/e 174.0270, 176.0240; found m/e 174.0272, 176.0238. Compound 67: $^1\text{H}$ NMR (CDCl$_3$) δ 0.9-1.6 (m), 1.7-2.2 (m), 2.20 (s), 2.23 (s), 2.68 (d, J=1.8 Hz), 5.4-6.2 (m). $^{13}\text{C}$ NMR (CDCl$_3$) δ 14.27, 15.24, 22.23, 22.66, 27.27, 28.08, 32.47, 124.35, 124.73. Mass spectrum calculated for C$_9$H$_{14}$S$_2$: m/e 186.0537, 188.0495; found m/e 186.053, 188.0490. Compound 68: $^1\text{H}$ NMR (CDCl$_3$) δ 0.84 (t, J=3.6 Hz), 1.4-1.6 (m), 2.07 (s), 2.0-2.48 (m), 5.23 (d, J=14.8 Hz), 5.91 (d, J=6.1 Hz), 6.16-6.32 (m). $^{13}\text{C}$ NMR (CDCl$_3$) δ 14.71, 32.96, 34.08, 107.78, 130.56, 139.05. Mass spectrum calculated for C$_8$H$_{10}$S: m/e 138.0503, 140.0461; found m/e 138.0505, 140.0462. Compound 69: $^1\text{H}$ NMR (CDCl$_3$) δ 1.93 (s, 3H), 3.60 (s, 2H), 7.17 (s, 5H). $^{13}\text{C}$ NMR (CDCl$_3$) δ 14.86, 38.37, 126.86, 128.42, 128.81, 138.32. Compound 70: $^1\text{H}$ NMR (CDCl$_3$) δ 2.33 (s, 3H), 2.45 (s, 3H), 7.0-7.24 (m, 4H). $^{13}\text{C}$ NMR (CDCl$_3$) δ 15.40, 19.88, 124.74, 125.20, 126.46, 129.83, 136.03, 137.68.
Reaction of 16 with potassium t-butoxide and methanethiol in dimethyl sulfoxide for 1 hour. The reaction proceeded as above for 1 hour. Work up afforded 1.92 g (from 2.0 g of 16) crude product. The product ratio was as follows: 66 (42.2%), 67 (17%), 68 (8.9%), and the three component mixture (32%).

Reaction of 7,7-dichlorobicycle[4.1.0]heptane (73) with potassium t-butoxide and methanethiol in dimethyl sulfoxide. The general procedure was used. The dichloride (73) (1.0 g, 6.1 mmol) in dimethyl sulfoxide (10 ml) was added to a stirred solution of methanethiol (1.46 g, 30.3 mmol) and potassium t-butoxide (8.16 g, 72.7 mmol) in dimethyl sulfoxide (30 ml). The resulting mixture was then stirred for 3.5 hours. Work up afforded 1.04 g crude product. GC analysis (5% Carbowax 20M on Chromosorb W AW) showed two products, 74 (36%) and 75 (64%). Purification was accomplished by preparative thin layer chromatography (hexane). Compound 74: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.2-2.24 (broad m), 2.15 (s), 3.37 (d, J=7.6 Hz), \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.50, 18.96, 20.96, 21.93, 23.44, 27.25, 46.61. Mass spectrum calculated for \(C_8H_{13}ClS\): m/e 176.0426; found m/e 176.0424. Compound 75: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.04 (s), 1.2-1.5 (m), 2.0-2.3 (m), 2.19 (s). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.23, 22.08, 26.71, 32.42, 34.91. Mass spectrum calculated for \(C_9H_{16}S_2\): m/e 188.0693, 190.0684; found m/e 188.0691, 190.0681.
Reaction of 7,7-dichlorodibenzo[a,c]bicyclo[4.1.0]heptane (76) with potassium t-butoxide and methanethiol in dimethyl sulfoxide. The general procedure was used. The dichloride (76) (1.0 g, 3.8 mmol) in dimethyl sulfoxide (30 ml) was added to a stirred solution of methanethiol (0.92 g, 19 mmol) and potassium t-butoxide (5.16 g, 46 mmol) in dimethyl sulfoxide (30 ml). The resulting mixture was stirred for 2 hours. Work up afforded 1.03 g (95% yield) crude product. NMR analysis showed a mixture of 77 and 78 in a ratio of 3 to 1. Compound 77 was purified by recrystallization from pentane. Compound 78 was purified from the filtrate by preparative thin layer chromatography (hexane/CHCl₃ 7/1). Compound 77: \(^1\)H NMR (CDCl₃) δ 0.76 and 1.83 (AB quartet, J=5.4 Hz), 2.13 (s), 7.1-7.48 (m), 7.92-8.16 (m), 8.28-8.46 (m). \(^{13}\)C NMR (CDCl₃) δ 16.32, 26.32, 43.30, 123.34, 126.90, 128.07, 129.88, 130.32, 135.39. Compound 78: \(^1\)H NMR (CDCl₃) δ 1.82 and 2.87 (AB quartet, J=5.4 Hz), 2.05 (s), 2.26 (s), 7.16-7.48 (m), 7.84-8.04 (m), 8.12-8.26 (m). \(^{13}\)C NMR (CDCl₃) δ 14.71, 16.86, 38.42, 40.18, 123.34, 127.05, 127.93, 128.27, 128.95, 133.73. Mass spectrum calculated for C₁₇H₁₆S₂: m/e 284.0693, 286.0651; found m/e 284.0691, 286.0655.

2,3-Dimethylene-1,2,3,4-tetrahydronaphthalene (85). Compound 85 was prepared by an improved method of Thummel's. A pyrolysis apparatus was constructed from a 20 inch long by 3/4 inch diameter Pyrex tube. The tube was packed with 10 inches of 6 mm glass beads and wrapped (12
inches) with a heating tape (8 feet by 1 inch). A small diameter tube held in place adjacent to the reaction tube by the heating tape held a thermocouple for temperature measurement. At the top of the tube was a 25 ml pressure-equalizing addition funnel. At the bottom was a 250 ml flask cooled to -78°C. The tube was heated to 310°C and 1,4-dihydronaphtho[b]cyclobutene (86) (1.46 g, 9.3 mmol, 80% pure, containing 20% naphtho[b]cyclobutene) in xylenes (20 ml) was added to the addition funnel. The solution was added dropwise over 30 min with a slight stream of nitrogen. After cooling to room temperature, the column was rinsed with CH₂Cl₂ (25 ml). Solvent removal in vacuo afforded 1.23 g (85% yield, 80% pure, containing 20% naphtho[b]cyclobutene) of a white solid. ¹H NMR (CDCl₃) δ 3.54 (s, 4H), 4.95 (m, 2H), 5.38 (m, 2H), 7.14 (s, 4H). Compound 85 was used without purification.

1-Bromo-2-chlorocyclopropene (84). 1-Bromo-1-trimethylsilyl-2,2-dichlorocyclopropane (88) (922 mg, 0.66 ml, 3.5 mmol) was added via syringe to a solution of n-tetrabutylammonium fluoride in tetrahydrofuran (1M, 3.5 ml, 3.5 mmol) cooled to -30°C. The mixture was stirred at ca. -20°C for 1 hour, after which time the solution had darkened considerably. The flask was cooled to -40°C and the solvent and volatile products were vacuum distilled into a liquid N₂ cooled trap containing the diene. It was necessary for the reaction flask to warm to room temperature and the pressure to be ca. 0.1 mm Hg for all
of the cyclopropene to distill.

**1a-Bromo-9a-chloro-la,2,3,8,9,9a-hexahydro-1H-cycloprop[b]anthracene** (89). A solution of the diene (85) (0.5 g, 3.2 mmol, 80% pure) and 1-bromo-2-chlorocyclopropene (84) (3.5 mmol) generated as above were stirred at -20°C for 1 hour. The reaction mixture was stored at -20°C overnight. CH₂Cl₂ was then added to dissolve most of the solids. TLC (hexane) indicated little diene present. The mixture was stirred at -20°C for an additional hour before warming to room temperature. The solvent was removed in vacuo. The residue was taken up in CH₂Cl₂, dried over MgSO₄, and the solvent removed in vacuo affording 0.76 g (76% yield) of a slight yellow solid. Purification of 89 was accomplished by column chromatography on silica gel (benzene, hexane) and recrystallization from pentane, m.p. 147-148°C. ¹H NMR (CDCl₃) δ 1.24-1.68 (m, 2H), 2.60-3.36 (m, 8H), 7.14 (s, 4H). Mass spectrum calculated for C₁₅H₁₄BrCl: m/e 307.9967, 311.9918; found m/e 307.9973, 311.9925.

**1a-Bromo-9a-chloro-la,2,9,9a-tetrahydro-1H-cycloprop[b]anthracene** (90). A solution of 89 (650 mg, 2.1 mmol) was stirred with DDQ (715 mg, 3.15 mmol) in CH₃Cl (50 ml) at room temperature for 20 hours. The mixture was filtered and the residue washed with CH₂Cl₂. The solvent was removed in vacuo to afford a black solid. The solid was passed through a short silica gel column (CH₂Cl₂) affording 410 mg (64% yield) of a yellow
solid. Purification of 90 was accomplished by column chromatography on silica gel (benzene, hexane) and recrystallization from pentane, m.p. 140-141°C. \(^1\)H NMR (CDCl\textsubscript{3}) \(\delta\) 1.34 (s, 2H), 3.5-4.0 (m, 4H), 7.25-7.6 (m, 4H), 7.6-7.9 (m, 2H). Mass spectrum calculated for C\textsubscript{15}H\textsubscript{12}BrCl: m/e 305.9811, 309.9761; found m/e 305.9813, 309.9766.

\(^1\)H-Cycloprop[b]anthracene (28). A solution of 90 (51.5 mg, 0.167 mmol) in tetrahydrofuran (0.75 ml) was added via syringe to a slurry of potassium \(\varepsilon\)-butoxide (136 mg, 1.2 mmol) in tetrahydrofuran (3 ml) cooled to \(-78^\circ\)C. The reaction mixture immediately turned black. After warming to \(-30^\circ\)C over a 30 min period, the solvent was removed by vacuum distillation (flask at room temperature). The residue was extracted with pentane (2 x 10 ml). The organics were centrifuged to remove inorganic salts and the solvent removed in vacuo to yield 13.2 mg (41.5% yield) of a slight yellow solid. \(^1\)H NMR (CDCl\textsubscript{3}) \(\delta\) 3.56 (s, H\textsubscript{1}, H\textsubscript{1}), 7.34-7.60 (AA'BB', H\textsubscript{5}, H\textsubscript{6}), 7.67 (s, H\textsubscript{2}, H\textsubscript{9}), 7.86-8.12 (AA'BB', H\textsubscript{4}, H\textsubscript{7}), 8.41 (s, H\textsubscript{3}, H\textsubscript{8}). \(^{13}\)C NMR (CDCl\textsubscript{3}) \(\delta\) 18.6 (C1), 111.6 (C2, C9), 123.3 (C1a, C9a), 125.3 (C5, C6), 126.6 (C4, C7), 128.1 (C3, C8), 131.7 (C3a, C7a), 135.2 (C2a, C8a). Ultraviolet spectrum \(\lambda_{\text{max}}\) 252 (c17,000). Mass spectrum calculated for C\textsubscript{15}H\textsubscript{10}: m/e 190.0783, 191.0816; found m/e 190.0781, 191.0816.

3,8-Dihydro-1H-cycloprop[b]anthracene (91). A solution of 89 (30 mg, 0.097 mmol) in tetrahydrofuran (0.5 ml) was added via syringe to a
stirred slurry of potassium t-butoxide (ca. 75 mg) in tetrahydrofuran (2 ml) cooled to -78°C. The reaction mixture darkened slowly upon warming to -20°C. The mixture was then cooled to -40°C and the solvent removed under reduced pressure. The residue was extracted with pentane, the mixture centrifuged and the solvent removed in vacuo to afford 18.6 mg (100% yield) crude product. ¹H NMR analysis indicated 77% of compound 91 and 23% of 2-methylanthracene (92). Compound 91 decomposed on standing at -20°C for 36 hours. Compound 91: ¹H NMR (CDCl₃) δ 3.27 (s, H₁, H₁'), 3.95 (s, H₃,H₈), 7.0-7.5 (m, 6H). Compound 92: ¹H NMR (CDCl₃) δ 2.53 (s, -Me), 7.6-8.4 (m).

1-Hydroxy-1-vinyl-1,2,3,4-tetrahydronaphthalene (96). Magnesium (8.31 g, 0.34 mol) and tetrahydrofuran (enough to cover the solid) were placed in a 1-liter flask fitted with a mechanical stirrer, addition funnel and a dry ice/acetone condenser. Vinyl bromide (40.2 g, 26.9 ml, 0.38 mol) in tetrahydrofuran (50 ml) was added to the addition funnel and 5 ml of the solution was added. A small crystal of I₂ was added and the flask heated on a steam bath until the reaction proceeded. The solution was then added dropwise to maintain a slight reflux without external cooling. After the addition was completed, the mixture was refluxed for 30 min. The flask was cooled to room temperature and the dry ice/acetone condenser was replaced with an ice water condenser. α-Tetralone (25 g, 0.17 mol) in tetrahydrofuran (75 ml) was added dropwise to maintain a reflux over 45 min. The mixture was then
refluxed for an additional 30 min. Saturated NH₄Cl (50 ml) was then added. The salts were dissolved, the layers were separated and the aqueous layer extracted with ether (2X). The combined organics were washed with brine (1X), dried over MgSO₄ and the solvent removed in vacuo. Purification was accomplished by vacuum distillation, b.p. 84–86 °C at 0.1 mm Hg, yielding 26.3 g (88% yield) of 96.

1-Vinyl-3,4-dihydronaphthalene (95). Iodine (364 mg, 1.4 mmol, 5 mol%) was added to a solution of 96 (5.0 g, 28.7 mmol) in toluene (200 ml). The mixture was heated at 100 °C for 1 hour. TLC showed product formation and very little starting material or polymer (polymer yield increased with a concentrated reaction solution). The organics were washed with Na₂S₂O₃ (2X), brine (1X), dried over MgSO₄ and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel (hexane). The product was then taken up in pentane to remove a solid polymer. Solvent removal in vacuo afforded a clear oil, 2.87 g (64% yield) contaminated with a slight amount of 1-vinylnaphthalene. Compound 95: ¹H NMR (CDCl₃) δ 2.12–2.42 (m, 2H), 2.56–2.92 (m, 2H), 5.08–5.68 (m, 2H), 6.18 (t, J=5 Hz, 1H), 6.42–6.84 (m, 1H), 7.0–7.6 (m, 4H).

1a-Bromo-9a-chloro-1a,1b,2,3,8,9a-hexahydro-1H-cyclopropa[a]-phenanthrene (97) and isomer. Compound 97 was prepared using the same procedure as that for 89. The diene (78) (0.50 g, 3.2 mmol) was reacted
with the cyclopropene (84) generated from 88 (922 mg, 3.5 mmol) and n-tetrabutylammonium fluoride in tetrahydrofuran (1M, 3.5 ml, 3.5 mmol) at -20°C. The solvent was removed in vacuo after drying to afford 0.84 g (85% yield) of 97. Column chromatography on silica gel (benzene, hexane) afforded 97 as a pair of isomers. ¹H NMR (CDCl₃) δ 1.00-1.92 (m), 2.36-2.72 (m), 2.72-3.32 (m), 6.00-6.32 (m), 7.00-7.32 (m), 7.40-7.72 (m). Mass spectrum calculated for C₁₅H₁₄BrCl: m/e 307.9967, 311.9918; found m/e 307.9973, 311.9910.

2,3-Dihydro-1H-cycloprop[a]phenanthrene (94). Compound 97 (30 mg, 0.097 mmol) in tetrahydrofuran (0.5 ml) was added via syringe to a mixture of potassium t-butoxide (ca. 75 mg) in tetrahydrofuran (2 ml) cooled to -78°C. The mixture was warmed to -10°C before re-cooling to -40°C. The solvent was then removed under reduced pressure. The residue was extracted with pentane (2X) and the solvent removed in vacuo affording 16.1 mg (87% yield) of pure 94. ¹H NMR (CDCl₃) δ 2.90 (s, 4H, H₂, H₃) 3.26 (s, H₁, H₁), 7.12-7.40 (m, 4H), 7.56-7.80 (m, 2H).
References and Notes


44. Reed, L. E.; Billups, W. E. unpublished results.


48. I thank B. E. Arney, Jr. of this laboratory for supplying the precursor to 1-bromo-2-chlorocyclopropene.


50. I thank W. A. Rodin of this laboratory for supplying this compound.


53. The $^1$H NMR spectrum of anthracene displays an AA'BB' system at $\delta$ 7.32-7.6 and 7.86-8.16 and a singlet at $\delta$ 8.42. $^1$H-cyclopropa[b]naphthalene displays singlets
at δ 3.41 and 7.40 and an AA'BB' system at δ 7.18-7.88.

54. Anthracene itself displays the same ultraviolet spectrum with λ max 256 (ε 180,000).

55. 9,10-Dihydroanthracene exhibits an NMR singlet δ 3.94 for H₉, H₁₀.


58. 9,10-Dihydrophenanthrene exhibits an NMR singlet δ 2.86 for H₉, H₁₀.
2.5 to 7.5 μm in CCl₄
7.5 to 16 μm in CS₂
2.5 to 7.5 μm in CCl₄
7.5 to 16 μm in CS₂
Appendix I

Generation of Bicyclo[4.1.0]heptatrienes
Generation of Bicyclo[4.1.0]heptatrienes

W. E. Billups, Larry E. Reed, Edward W. Casserly, and L. P. Lin

Department of Chemistry, Rice University, Houston, Texas 77001

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Derivatives of bicyclo[4.1.0]heptatrienes have been generated in solution by the base-induced dehydrochlorination of germ-dichlorocyclopropanes. Reaction of 7,7-dichlorobenzene[4.1.0]heptatriene with potassium tert-butoxide in tetrahydrofuran at 0°C gives mainly products derived from solvent incorporation by carbene insertion. Evidence that the carbene results from rearrangement of the bicycloheptatriene derives from the successful interception of the bicycloheptatriene with nucleophile (MsS⁻, endo-7-Chlorobenzene[4.1.0]heptatriene failed to react with potassium tert-butoxide in tetrahydrofuran. Generation of benzo[bicyclo[4.1.0]heptatriene was also accomplished via the base-induced dehydrochlorination of germ-dichlorocyclopropane. 1-Methylbicyclo[4.1.0]heptatriene gives products derived from multiple carbene-cyclopropane rearrangements. In contrast, neopentylmethylbicycloheptatrienes generated by the dehydrochlorination route give only carbene-derived products resulting from the initially produced bicycloheptatriene.

The interconversion of phenyl carbene and its derivatives with bicycloheptatrienylides (eq 1) was first postulated by Shechter and Vander Stouw12 to account for the formation of styrene in the gas-phase pyrolysis of α-tolyldiazomethane. On the basis of analogy with the well-known interconversion of vinylcarbene and cyclopropane,12 these workers suggested that the rearrangement depicted in eq 1 probably proceeds via bicyclo[4.1.0]heptatriene (1) as a reactive intermediate. Although other

intermediates have been considered,1,2,12 only 1 seems to be consistent with all of the experimental observations.

The discrete existence of bicyclo[4.1.0]heptatriene 2 and 3 in solution was established by their


Generation of Bicyclo[4.1.0]heptatrienes

\[
\begin{align*}
6 & \rightarrow 8 \\
& \rightarrow 11 \\
10 & \rightarrow 12 \\
\end{align*}
\]

interception with furan and cyclopentadiene to give 4 and 5, respectively. \(^{11}\)

Simultaneously, work in our laboratory demonstrated that the dehydrochlorination of suitably substituted halocylopropanes provides a direct entry into the bicyclo[4.1.0]heptatriene ring system. \(^{2,3,4}\) The dehydrohalogenation route is attractive since the bicycloheptatriene can be generated at or below room temperature in solution and in the absence of radiation, which assures that excited states are not involved. In addition, the method promises to provide simple nonirradiated derivatives which, heretofore, have not been generated in solution.

The adduct of dichlorocarbene and phenanthrene, 7,7-dichlorocycloheptatriene \(^{2}\), was chosen for our initial studies. Treatment of 6 with a suspension of potassium tert-butoxide (2 equiv) in tetrahydrofuran at 0°C gives a viscous oil identified as 7 (mixture of diastereomers).

The formation of 7 can be rationalized by invoking bicycloheptatriene 8 as a reactive intermediate, which rearranges to carbene 9 followed by insertion into the solvent (Scheme I). In principle, however, the carbene could be derived directly from 6 as shown in Scheme II. The formation of solvent-insertion product can, of course, be taken as evidence for the carbene.

Fortunately, nucleophile trapping experiments such as those employed by Shields and Gardner\(^{18}\) provide a method to trap 8. The result of an experiment in which methyl mercaptoacetate is used as the trapping reagent is illustrated in Scheme III. It is interesting that in addition to the expected bicycloheptatriene 8, one must also invoke 10, which arises from elimination of HCl from the intermediate adduct 11. Both bicycloheptatrienes must be sufficiently long lived to experience addition of the nucleophile. On the other hand, bicycloheptatriene 8, in the absence of a trapping reagent, rearranges at 0°C to give the arylcarbene, a species normally considered to be a high-energy one. The strain in 8 and the increase in resonance energy upon ring opening are probably sufficient to place the carbene at lower energy than the cyclopropene. These observations are consistent with other examples of low-temperature arylcarbene → bicycloheptatriene rearrangement. \(^{11}\)

We did not observe insertion products arising from cycloheptatrienylidene 13, but this is not surprising since the bicycloheptatriene → cycloheptadienylidene rearrangement normally occurs at a much higher temperature (250–400 °C). \(^{19}\)

Experiments with 14, prepared from 9-methylphenanthrene and dichlorocarbene, afforded none of the expected solvent insertion product 15 but only an amorphous solid which failed to yield characteristic products despite extensive efforts with column and thin-layer chromatography.

Evidence for the expected bicycloheptatriene is found, however, in the reaction of 14 with potassium tert-butoxide in the presence of methyl mercaptoacetate which yields adduct 16 in 92% yield, eq 2. Although two stereoisomers of 16 are possible, a single set of three signals at \(\delta 1.87\) (3 H), 2.94 (3 H), and 3.52 (1 H) in the nonsymmetric region of the \(^1\)H NMR spectrum suggested that only one isomer was produced. Using 17 as a model, one can reasonably assume that the single cyclopropyl hydrogen resides in the exo
position since the endo-hydrogen of 17 is strongly shielded by overlap with the two aromatic rings. This stereochemical assignment is also consistent with previous observations that nucleophiles add syn to cyclopropenyl double bonds.\(^{16}\)

The lithium aluminum hydride reduction of 6 afforded a single isomer (eq 3) identified as 18 (90% yield) by the NMR chemical shift and coupling constant of the cyclopropyl hydrogens: \(\delta\ 2.87\) (d, \(J = 8.0\) Hz, 2 H), 3.86 (t, \(J = 8.0\) Hz, 1 H).

Surprisingly, compound 18 fails to react even after 1 week with potassium tert-butoxide in either tetrahydrofuran or dimethyl sulfoxide. Apparently, dehydrochlorination of 18, as in other rigid cyclic and bicyclic systems in which an anti-periplanar relationship of leaving groups cannot be adopted, proceeds via syn-periplanar transition states.\(^{18}\)

A second example illustrating the dehydrochlorination route to bicycloheptatriene is found in the naphthalene system. Our initial studies were carried out with 19 which was prepared in the straightforward approach shown in eq 4.

Treatment of 19 with potassium tert-butoxide in tetrahydrofuran afforded a tarlike substance which was subjected to column chromatography (silica gel, hexane) to yield 1-naphthaldehyde (26) in 10% yield and a diastereomeric mixture of solvent insertion products 21 in 20-45% yield, eq 5. We have assigned structure 21 as the 1-substituted naphthalene (rather than substitution in the 2-position) on the basis of the following observations: (1) compound 20 probably arises from the same carbons that gives the solvent insertion product (Scheme IV); (2) the NMR spectrum of the ether reveals that one of the aromatic protons is deshielded more than the remaining six, typical of 1-substituted naphthalenes.

We were not able to characterize products from the reaction of 19 with potassium tert-butoxide and methyl mercaptide. However, when methoxide was used as nucleophile, adduct 22 was isolated in 41% yield, eq 5. The mechanism of formation of 22 is puzzling, and rationalization in terms of a bicycloheptatriene is difficult.

Precursor 23 was prepared in 85% yield from 1-methyl-5,4-dihyrdronaphthalene and dichlorocarbene, eq 7. The methyl group in 23 serves a dual purpose, first, to act as a label to detect rearrangement and second to simplify the base-induced elimination sequence by replacement of the more acidic benzylic hydrogen.

Treatment of 23 as shown in eq 6 afforded, after preparative TLC, unreacted starting material (59%) and tert-butyli ethers 24 and 25 (eluting together, 43% combined yield) in a ratio of 3:2, respectively. Ethers 24 and 25 were separated by preparative GLC, and 24 was identified by comparison of its spectral and chromatographic properties with those of an authentic sample (see Experimental Section). The spectral properties of 25 reveal that it is an isomer of 24, but an unambiguous synthetic route to 25, as a structure proof, was not obvious. However, the formation of isomers other than 24 and 25 can be pre-


Generation of Bicyclo[4.1.0]heptatrienes

Scheme V

\[
\begin{align*}
\text{Me} & \quad \text{Cl} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Cl} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

at 350 °C.²¹ Formation of 32 and 33 would, of course, be energetically unfavorable since bond delocalization is lost in both rings.

The reaction of naphthylcarbene 28 and 31 with tert-butoxide to afford the tert-butyl ethers is expected, since electrophilic carbene are known to react readily with alcohoxides.²² The failure of 29 to react with tert-butoxide is attributed to the nucleophilicity of this species.²³²⁴ It is interesting that naphth[o]cyclobutene (34) was not formed, although it is the only product detected when 28 is generated in the gas phase.²³

In contrast to the aryliclorobenzenes, solvent-insertion products were not observed. We have found that, in general, aryliclorobenzenes usually give solvent insertion products, whereas aryliclores react with nucleophiles. An attempt to trap 27 (or 35) by dehydrochlorination in the presence of nucleophile (MeS) afforded only 35 (~100%), derived from the initially formed cyclopropane (eq 9). The stereochemistry (syn addition) was assigned from the chemical shift of the cyclopropyl proton (δ 2.50) by using compounds 16 and 17 as models.

Several other experiments to trap the intermediates of Scheme V were also unsuccessful. Thus, no cycloadducts of 27 or 36 were isolated when 1,3-diphenylbenzoxa-

furan²⁵ was added to the reaction medium. Furthermore, it was not possible to detect adduct 36 when styrene was added, although electrophilic olefins have been used previously to intercept cycloheptatrienylides.²⁶

Generation of nonannelated bicyclo[4.1.0]heptatrienes via the elimination route is especially interesting since it has not been possible to prepare members of this series in solution. In analogy to the generation of 27 from 23, compound 37 is attractive as a precursor to 38. The methyl group is necessary since the dichlorocarbene adduct of 1,3-cyclohexadiene itself is known to give benzo
cyclopropane under the reaction conditions.²⁷ The key step in the synthesis of 37 is the formation of 2-methyl-1,3-cyclohexadiene from the tosylhydrazones by the Shapiro modification²⁸ of the Ramford-Stevens reaction. The desired precursor, 37, was produced in 14%

(25) We thank Professor R. Thummel for providing a sample of naphth[a]cyclobutene.
overall yield and free of its isomer 39, as determined by gas chromatography.

Treatment of 37 with potassium tert-butoxide in tetrahydrofuran afforded, in addition to unreacted starting material (11.5%), o-methylbenzyl tert-butyI ether (40) in 40.5% yield, eq 10. A trace of what is probably a benzocyclopropene derivative was also detected by the characteristic foul odor that is associated with benzocyclopropene and its derivatives.

In order to detect small amounts of the meta and para isomers that might have formed via rearrangement, authentic samples of xyllyl tert-butyl ethers 41 and 42 were prepared by sovolysis of the respective methylbenzyl bromides. Surprisingly, it was not possible to resolve these isomers chromatographically. Even columns which resolved the three xylenes were ineffective for the separation of the others.

By use of nuclear magnetic resonance spectroscopy (EM-390, 50-fold expansion), the tert-butyl peaks could be resolved, but the methylene and methyl peaks remained unresolved. The product obtained from eq 10 showed only one tert-butyl resonance and had an infrared spectrum identical with authentic 40, prepared from sovolysis of o-methylbenzyl bromide.

The formation of 40 can then be rationalized as shown in Scheme VI. The poor mass balance is perhaps an indication that some of the products are not stable to the reaction conditions. One might speculate that these could be derived from the aromatic carbene (perhaps dimer) and would most likely be unstable to the long reaction time required for the consumption of 37. The absence of methylcarbene-derived products (41, to a limit of detection of ca. 5% of 40) indicates that rearrangement of 38 to 43 (if it occurs) is irreversible (eq 11).

Experimental Section

General Methods. Proton magnetic resonance spectra were recorded in CDCl₃ on a Varian Model EM-390 (90 MHz), XL-100 (100 MHz), or A66/60 (60 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from internal MeSi. Infrared spectra of liquids were taken on neat compounds held between sodium chloride plates with a Beckman IRE spectrophotometer. High-resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer operated at 70 eV. A Finnigan Model 3300 gas chromatography/mass spectrometer was used to record low-resolution mass spectra. A Hewlett-Packard Model 700 gas chromatograph with a thermal conductivity detector and operated with a flow rate of 60 mL/min was used for all analytical and preparative GLC. GLC column designations are as follows: (A) 4 ft x 1/4 in., 20% OV-17 on Chromosorb W-DMCS; (B) 6 ft x 1/8 in., 20% Apiezon L on Chromosorb W-DMCS; (C) 4 ft x 1/8 in., 10% Carbowax 20M on Anakrom AB; (D) 4 ft x 1/4 in., 16% SE-30 on Chromosorb WAW; (E) 4 ft x 1/4 in., 20% SE-30 on Chromosorb PAW. All melting points and boiling points are uncorrected.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl immediately before use. Dimethyl sulfoxide (Me₂SO) was distilled from calcium hydride under reduced pressure and stored over precondensed 4A molecular sieves. Column chromatography was performed on Baker reagent grade silica gel (60-200 mesh). Merck precoated silica gel plates were used for analytical (100 x 20 cm) and preparative (200 x 20 cm x 2 mm) thin-layer chromatography. All other chemicals were of reagent quality and used as obtained from the suppliers.

Reaction of 7,7-Dichlorodibenzo[a,j]bicyclo[4.1.0]heptane (6) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 6 (0.61 g, 0.01 mol) in 20 mL of tetrahydrofuran was added under nitrogen to a chilled suspension of potassium tert-butoxide (2.35 g, 0.02 mol) in tetrahydrofuran (60 mL). The mixture was stirred at 0 °C for 18 h and then worked up by adding 500 mL of water and 50 mL of chloroform. The organic layer was separated, washed several times with water, and dried over sodium sulfate, and the solvent was removed in vacuo. Purification by column chromatography (silica gel, chloroform) gave 2.29 g of 7 (31% yield of diastereomers by NMR). Further purification was achieved by preparative thin-layer chromatography (silica gel, chloroform): NMR δ 7.02-7.20 (m, 4 H), 4.90-4.80 (m, 1 H), 2.60-2.30 (s, 4 H). The major diastereomer exhibits a doublet at 6.85 (J = 5 Hz) while the remaining diastereomer exhibits the doublet at 5.63 (1 H, J = 5 Hz), 7.30-8.60 (m, 9 H), 1H 10.50 (s), 1480 (s), 1350 (s), 745 (s) cm⁻¹ mass spectrum, m/z 298.0884 (M⁺, calcd 298.087).
Generation of Bicyclo[4.1.0]heptatrienes

of (2.61 g, 0.01 mol) in 60 mL of dimethyl sulfide. The mixture was stirred at room temperature for 3 h and then poured into water. The resulting solution was extracted with chloroform. After removal of solvent, 12 was isolated as a yellow solid. Decoloration with charcoal and recrystallization from acetone gave 7.8 mg (yield 0.2%) of colorless material. mp 146–149 °C; NMR δ 1.21 and 1.61 (AB q, J = 5.0 Hz, 2 H, cyclopropyl), 2.1 (s, 5 H, Me), 7.1–7.8 (m, 4 H, aromatic), 7.8 (s, 1 H, aromat), 8.25 (s, 1 H, aromat); IR 2920 (v, CH₃), 2900, 2860, 2130, 1630, 1500, 1470, 1360, 1230, 1010, 930, 840 (cm⁻¹). Found: C, 79.42; H, 6.56. Calc. for C₁₆H₁₇N: C, 79.54; H, 6.49.

7,7-Dichloro-1-methylbicyclo[4.1.0]heptane (14). A solution of 30% aqueous sodium hydroxide (16 mL, 0.2 mol) was added dropwise at 0 °C to a stirred solution of 7-methylbicycloheptatriene (4.0, 0.15 mol) and cyclotrimethylsilane (0.07 ml, 0.52 mmol) in chloroform (16 mL). The resulting mixture was stirred for 2 h at room temperature and then poured into 100 mL of water and extracted with chloroform (2 x 50 mL) to afford 7.5 mg (0.06%) of 7,7-dichloro-1-methylbicyclo[4.1.0]heptane (14) as a white solid. mp 55–56 °C; NMR δ 1.12 and 3.49 (AB q, J = 6 Hz, 2 H, cyclopropyl), 3.30 (s, 6 H, SO₂Me), 7.22–7.47 (m, 4 H, aromatic), 7.50–7.63 (m, 4 H, aromatic). Anal. Calc. for C₁₄H₂₂Cl₂N: C, 69.64; H, 7.40. Found: C, 69.14; H, 7.43.

Reactions of 7,7-Dichloro-1-methylbicyclo[4.1.0]heptene (15) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 15 (1.2 eq.) was treated with tert-BuOK (1.6 eq.) in THF at 0 °C. Work-up by thin-layer chromatography failed to provide characteristic products.

7,7-Dichloro-1-methylbicyclo[4.1.0]heptane (14) (19) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 19 (21.1 g, 72.3 mmol) in tetrahydrofuran (8 mL) was added under nitrogen to a suspension of potassium tert-butoxide (22.4 g, 21.8 mmol) in tetrahydrofuran (25 mL). The solution was maintained at 0 °C throughout the addition. The reaction mixture was stirred at 0 °C for 2 h, then poured into water (300 mL), and extracted with chloroform (2 x 50 mL). The combined extracts were washed with brine (100 mL) and dried over MgSO₄. Solvent removal in vacuo gave a black tar which was subjected to column chromatography (silica gel, hexane) to yield 10.7 mg (10% yield) of 1-naphthaldehyde (29), one diastereomer of 21 (134.5 mg, 8% yield), and the remaining isomer 21 (150.5 mg, 10% yield). When the reaction was run on a larger scale, the yield of 21 was 45%: NMR (CCl₄) δ 1.50–2.10 (m, 4 H), 3.65–3.97 (m, 2 H), 4.20–4.68 (m, 1 H), 5.60–6.20 (2 H, 6.53 and 5.83), 1.13 (s, J = 6.5 Hz), 7.32–7.52 (7 H, 7 Hz); IR (mat) 3090 (s), 2900 (s), 2870 (s), 1595 (s), 1010 (s), 1000 (s), 745 (s) cm⁻¹.

Reactions of 7,7-Dichloro-1-methylbicyclo[4.1.0]heptane (15) with Potassium tert-Butoxide and Methanol in Dimethyl Sulfoxide. Compound 15 (19.2 g, 100 mmol) was added to a mixture of potassium tert-butoxide (60.4 g, 0.55 mol) and methanol (9.63 g, 0.20 mol) in dimethyl sulfoxide (70 mL), and the mixture was stirred under nitrogen at room temperature for 18 h. Work-up and purification by column chromatography provided 0.89 g (41% yield) of 22: NMR δ 3.04 (s, 2 H), 2.38 (s, 3 H), 2.39 (s, 3 H), 2.77 (s, 2 H), 1.7–7.4 (m, 7 H), 7.6–8.1 (m, 2 H), 8.2–8.4 (m, 1 H); mass spectrum, m/e 286.0335. 1H NMR: δ 7.57–7.74 (m, 4 H), 7.37–7.47 (m, 1 H), 7.8–8.1 (m, 2 H), 8.2–8.4 (m, 1 H); mass spectrum, m/e 286.0358. 7,7-Dichloro-1-methylbicyclo[4.1.0]heptene (16) with Lithium Alumina Hydride. A solution of 16 (2.21 g, 10.4 mmol) in dry ether (60 mL) was added dropwise to a suspension of lithium aluminum hydride (4.8, 0.13 mol) in ether (40 mL). The mixture was refluxed 2 h and then worked up by the dropwise addition of water (2.7 mL), 10% sodium hydroxide solution (100 mL), and then water (0.1 mL). The inorganic salts were then removed by filtration, and the filtrate was concentrated in vacuo to yield 1.41 g (60% of 16: mp 142–144 °C (after recrystallization from chloroform); NMR δ 0.81 (d, J = 8.0 Hz, 2 H, 2.36 (s, 3 H), 2.77 (s, 3 H), 1.7–7.4 (m, 4 H), 7.8–8.1 (m, 2 H); mass spectrum, m/e 226 (M⁺, 26%). Anal. Calc. for C₁₁H₁₂Cl₂: C, 70.67; H, 7.40. Found: C, 70.91; H, 7.49.

Attempted Reaction of 7-Chlorobicyclo[4.1.0]heptene (18) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 18 (565 mg, 2.2 mmol) in dry tetrahydrofuran (8 mL) was added dropwise under N₂ to a stirred suspension of potassium tert-butoxide (501 mg, 4.5 mmol) in tetrahydrofuran (15 mL). The temperature was maintained at 0 °C during the addition. The reaction mixture was stirred for 16 h at room temperature, poured into water (50 mL), extracted with ether (100 mL), dried over MgSO₄, and evaporated in vacuo to afford 400 mg of white solid which was shown to be starting material by comparison of NMR spectra and TLC properties. Starting material was also recovered when 18 was treated with 16 equiv of potassium tert-butoxide for 7 days.

Attempted Reaction of 7-Chlorobicyclo[4.1.0]heptene (18) with Potassium tert-Butoxide and Methyl Mercaptan in Dimethyl Sulfoxide. Compound 18 (665 mg, 2.9 mmol) in dimethyl sulfoxide (15 mL) was added dropwise to a solution of potassium tert-butoxide (3.74 g, 24.4 mmol) and methyl mercaptan (0.52 g, 10.5 mmol) in dimethyl sulfoxide (15 mL). After the mixture was stirred for 3 h, water was added and the solution was extracted with ether (3 x 50 mL). The combined extracts were washed with water and dried over MgSO₄. Solvent evaporation afforded 670 mg (100%) of starting material.

7,7-Dichloro-1-methylbicyclo[4.1.0]heptene (19). 7,7-Dichloro-1-methylbicyclo[4.1.0]heptene (19) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 19 (21.1 g, 72.3 mmol) in tetrahydrofuran (8 mL) was added under nitrogen to a suspension of potassium tert-butoxide (22.4 g, 21.8 mmol) in tetrahydrofuran (25 mL). The solution was maintained at 0 °C throughout the addition. The reaction mixture was stirred at 0 °C for 2 h, then poured into water (300 mL), and extracted with chloroform (2 x 50 mL). The combined extracts were washed with brine (100 mL) and dried over MgSO₄. Solvent removal in vacuo gave a black tar which was subjected to column chromatography (silica gel, hexane) to yield 10.7 mg (10% yield) of 1-naphthaldehyde (29), one diastereomer of 21 (134.5 mg, 8% yield), and the remaining diastereomer of 21 (150.5 mg, 10% yield). When the reaction was run on a larger scale, the yield of 21 was 45%: NMR (CCl₄) δ 1.50–2.10 (m, 4 H), 3.65–3.97 (m, 2 H), 4.20–4.68 (m, 1 H), 5.60–6.20 (2 H, 6.53 and 5.83), 1.13 (s, J = 6.5 Hz), 7.32–7.52 (7 H, 7 Hz); IR (mat) 3090 (s), 2900 (s), 2870 (s), 1595 (s), 1010 (s), 1000 (s), 745 (s) cm⁻¹.
Reaction of 7,7-Dichloro-1-methylbenzene[a]bicyclo[4.4.0]decane (23) with Potassium tert-Butylate in Tetrahydrofuran. A solution of 23 (0.06 g, 0.007 mmol) in 2 mL of tetrahydrofuran was added dropwise to a stirred suspension of sodium tert-butyllate (2.01 g, 17.9 mmol) in dimethyl sulfoxide (20 mL). The mixture was stirred for 24 hours with an additional 3 mL of tert-butylate (2.516 mmol) in dimethyl sulfoxide (3 mL) added. After 1 hour, the reaction mixture was diluted with water (200 mL) and extracted with ether (3 X 20 mL). The combined ether phases were washed with water (200 mL) and dried over MgSO4. Solvent removal gave 332 mg (ca. 90% yield) of essentially pure 33: NMR 2.07 (s, 3H), 2.18 (s, 3H), 1.95-2.11 (s, 4H), 3.36 (t, 1H), 0.23-0.25 (s, 2H), 0.55 (s, 2H), 236.0681, 236.0683.

Attempted Reaction of 7,7-Dichloro-1-methylbenzene[a]bicyclo[4.4.0]decane (23) with Potassium tert-Butylate and Diphenylmethanesulfonate. A solution of 23 (17 mg, 0.074 mmol) in THF (2 mL) was added dropwise to a solution of diphenylmethanesulfonate (4.1 mg, 0.015 mmol) and potassium tert-butyllate (1.27 g, 11.5 mmol) in THF (3 mL). After being stirred at room temperature for 23 h, the reaction mixture was diluted with water (100 mL) and extracted with ether (3 x 25 mL). The combined ether phases were washed with water (2 x 100 mL) and brine (100 mL) and dried over MgSO4. Solvent removal in vacuo afforded a yellow solid which had no detectable impurities in the NMR spectrum. Preparative TLC (hexane-CH2Cl2, 1:1) afforded unreacted starting material (108 mg, 49%), ethers 23 and 24 (37 mg, 22%), and diphenylmethanesulfonate (319 mg, 85%).

Attempted Reaction of 7,7-Dichloro-1-methylbenzene[a]bicyclo[4.4.0]decane (23) with Potassium tert-Butylate and Stereoselective Elaboration. Compound 23 (302 mg, 1.35 mmol) in 3 mL of THF was added dropwise to a solution of potassium tert-butyllate (2.15 g, 18.3 mmol) and styrene (764 mg, 7.7 mmol) in THF (17 mL) at 0 °C. The mixture was stirred at 10-15 °C for 43 h, diluted with water (200 mL) and extracted with chloroform (100 mL). The combined ether phases were washed with water (2 x 100 mL) and brine (100 mL) and dried over MgSO4. The solvent and traces of styrene were removed by pumping at 0 mm Hg overnight. Preparative TLC (hexane-CH2Cl2, 1:1) afforded unreacted starting material (145 mg, 51%) and tert-butyll ether 24 and 25 (34 mg, 19%).

2-Methylcyclohexene Oxide. Freshly prepared 2-methylcyclohexene oxide (6.42 g, 0.05 mol) was added all at once to a refluxing solution of tolylbromine (0.13 g, 0.007 mol) in 60% aqueous methanol (17 mL). The reaction mixture was passed immediately in a refrigerator and allowed to stand for 6 days. The resulting solid was collected by filtration and recrystallized from absolute ethanol to afford 10.64 g (76.5% yield) of the tolylhydroxide, mp 158-160 °C (lit. 159.5-157 °C).

2-Methyl-3,3-cyclohexadiene. Metallithium (75 mL, 128 mmol) in ether was added dropwise to a solution of 2-methylcyclohexene oxide to afford a colorless solution of 2-methyl-3,3-cyclohexadiene (100 mL, 3.36 mmol) at -78 °C. After the mixture was stirred an additional 15 min at -78 °C, 1.3 mL (21.7 mmol) of methyl iodide was added dropwise. After 5 min, the cooling bath was removed and stirring continued an additional 1 h followed by dilution with water (50 mL) and extraction into ether (50 mL). The ether extract was washed with brine (50 mL) and dried over MgSO4. Solvent evaporation afforded 0.8 g of an orange oil. GLC (column B, 230 °C) indicated two components in the ratio 21:1. These were separated by preparative GLC and the minor component was identified with an authentic sample of 2-(tert-butyloxy)methylenephthalene by GLC coincidence and NMR, whereas the major one was identified with 24 obtained from 23, as shown by its IR and NMR spectra and by GLC coincidence (column B, 230 °C) and prep GLC (220 °C).
(m), calc 178. Anal. Calcd for C₁₈H₂₇Cl₃: C, 64.20; H, 5.69.

178 (m), calc 178. Anal. Calcd for C₁₈H₂₇Cl₃: C, 64.20; H, 5.69.

Reaction of 2,7-Dichloro-1-methylbicyclo[4.1.0]hept-2-ene (47) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 37 (0.51 g, 3.3 mmol) in tetrahydrofuran (90 mL) was added dropwise under nitrogen to a solution of potassium tert-butoxide (6.81 g, 49.3 mmol) in dry tetrahydrofuran (50 mL) which was maintained at 0 °C by means of an ice bath. After being stirred at room temperature for 72 h, the reaction mixture was diluted with water (100 mL) and extracted with ether (100 mL). The ether extract was washed with brine (100 mL) and dried over MgSO₄. Solvent evaporation in vacuo afforded 667.5 mg of dark brown oil which was shown by GLC (column A, 170 °C) to contain starting material (11.3% yield) and o-xylene tert-butyl ether (40; 40.5% yield). Compound 40 was isolated by preparative GLC and shown to be identical (IR and NMR) with an authentic sample. NMR 1.28 (s, 3 H), 2.20 (s, 3 H), 4.45 (q, 2 H), 7.20–7.20 (m, 5 H), 7.30–7.27 (m, 2 H), 7.30–7.20 (m, 1 H); mass spectrum, 178 (M⁺, calc 178).

Synthesis of o-, m-, and p-Xylyl tert-Butyl Ethers (40–43)

An authentic sample of each ether was prepared in >95% yield by reaction of the corresponding bromoxylene with potassium tert-butoxide in tetrahydrofuran for 12–20 h.

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Registry No. 6, 37688-28-9; 7 (isomer 1), 50568-17-9; 7 (isomer 2), 50568-38-8; 12, 50568-72-9; 12 diclorone, 72949-99-4; 14, 72949-00-5; 18, 72949-01-6; 18, 50563-21-5; 18, 60099-40-4; 22, 60-77-1; 21 (isomer 2), 72949-02-5; 21 (isomer 2), 76010-55-6; 22, 72949-03-6; 23, 60139-36-5; 24, 60139-35-1; 24, 60139-37-2; 24, 72949-04-1; 24, 72949-05-2; 40, 50563-32-0; 41, 40077-89-6; 42, 72949-06-3; pentafluorobenzene, 86-81-8; tetrahydrofuran, 109-96-6; methyl mercaptan, 74-90-1; 2-fluorophenanthrene, 863-30-6; 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptene, 60996-38-8; 1-methyl-3,4-dihydrobiphenyl, 6373-13-1; o-toluenone, 829-24-0; methyl isothiocyanate, 74-90-1; 1-bromomethyl-4-(bromomethyl)benzene, 37763-43-2; 1-bromo-2-methylacetophenone, 2286-65-1; 2-methylcyclobenzene, 72949-07-4; 2-methylcyclobenzene, 111-19-2; 2,3-dimethyl-1,3-cyclohexadiene, 1489-97-5; o-bromoxylene, 88-92-8; m-bromoxylene, 820-13-3; p-bromoxylene, 134-51-4.
Appendix II

Methyl Transfer Reactions. 7. System with CH₃SO⁺ Intermediate
Methyl-Transfer Reactions. 7. System with CH₃OSO⁺ Intermediate

J. Joseph Christie, Edward S. Lewis,* and Edward F. Casserly

Department of Chemistry, Rice University, Houston, Texas 77251

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Methyl chlorosulfide with anion tetraethyl disulfide initially at dry ice temperature is a very powerful methylation system. It methyllates sulfones, methyl chloride, and even some enantiomers of sulfuric acid.

The active methylation species is apparently the cation CH₃OSO⁺. Dimethyl sulfide is decomposed catalytically by methyl trifluoromethanesulfonate to dimethyl ether and sulfur dioxide, and the same cation appears to be intermediate. The mechanism includes an exchange of the methyl groups between the two esters, allowing a practical synthesis of methyl-Triflate. Dimethyl sulfide does not methylene detectably on sulfur.

Introduction

Powerful methylation agents are in principle compounds or ions with methyl attached to good leaving groups. Anionic leaving groups of exceptional stability are Cl⁻, F⁻, SO₃⁻, CH₃CN, NO₂⁻, or F⁻, which are listed in order of apparent increasing methylating power. However, still more powerful cationic methylation agents may be designed with neutral leaving groups; thus trimethylammonium ions are more powerful than trimethylammonium cation, although less so than triethylammonium cation. Dimethylhalonium ions are presumably more powerful than trimethylammonium cation, but even less nucophilic leaving groups than methyl halides are known. Notably, N₂F from CH₃N₂⁺ can leave in the system diazonium + acid, as well as in peracids stable diazonium salts. The system CH₃F⁺ + SF₅⁻ is perhaps as powerful as any well-characterized system, but one can conceive of other stable neutral molecule leaving groups, some of which may show reactions other than methylation, such as the known mass spectrometric species CH₃⁺, CH₃⁺, CH₃⁺, and CH₃⁺, in the gas-phase limit. CH₃⁺. In solution, however, the solvent will always be attached to methyl if there is not a better nucleophile in solution. Thus in the solvent S, no better methylation agent than CH₃OSO⁺ will exist at equilibrium, although (in contrast to the leveling effect of solvents on proton acidity) more powerful methylation agents than CH₃OSO⁺ may have transient stability, since the methyl-transfer reactions are often perceptibly slow. Thus it is possible to do alkylations in aqueous solution with cyclic halonium salts or with methyl triflate. In this paper we shall be concerned with the species CH₃OSO⁺ (J), which is formally the ultimate methylation agent in liquid SO₂ and can be made from SO₂ and a more powerful methylation agent. This has been realized, by the mixture of CH₃F⁺ + SF₅⁻ + SO₂, the ion C₄H₄OSO⁺ has been well identified in solution as a crystalline salt with the counter ion SF₅⁻. The use of CH₃F⁺, SF₅⁻, or CH₃N₂⁺ + acid are possible but expensive, inconvenient, and hazardous methods. Our approach has been to use the

(3) Lewis, E. S.; Smith, M. J.; Christie, J. J., previous paper in this issue.

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cheap and readily available methyl chloroformite and antimony pentachloride as a possible source of this cation and to study its methyla"tion power and other reactions. The same cation is implicated as an intermediate in the decomposition of dimethyl sulfoxide initiated by methylation.

We were also interested in dimethyl sulfoxide as a possible ambident nucleophile; methylation on sulfur has parallels in lower oxidation states and would be the first step in a potential rearrangement to methyl methanesulfonate, a sulfur analogue of the Arbuzov reaction.

**Results**

Methyl chloroformite, MeOSCI, is readily prepared from methanol and thionyl chloride; it is thus a cheap and very accessible reagent. Antimony pentachloride is an easily handled substance compatible with glass and about a tenth the price per mole of antimony pentfluoride. When methyl chloroformite is treated with antimony pentachloride at room temperature, a violent reaction giving methyl chloride and sulfur dioxide takes place, which can be modified by cooling and by dilution with thioryl chloride, which is very resistant to methylation. In this solvent at 78 °C the combination is reasonably stable, yet we believe the species CH$_2$OSO + SCl$_2$ is already formed. On warming, SCl$_2$ and SO$_2$ are produced, corresponding to a catalysis by SCl$_2$ of the decomposition of the chloroformite. We postulate a mechanism comprising reactions 1 and 2. Thus we

$$\text{CH}_2\text{OSO} + \text{SiCl}_4 \rightarrow \text{CH}_2\text{OSO} + \text{SiCl}_2$$  \hspace{1cm} (1)

$$\text{SiCl}_4 + \text{CH}_2\text{OSO} = \text{SiCl}_2 + \text{CHCl}_3 + \text{SO}_2$$  \hspace{1cm} (2)

and an electrophilic catalysis by the uncatalyzed and dechlorinated decomposition of chloroformites.

Reaction 2 attracted our attention because SCl$_2$ is not expected to be a very nucleophilic species; hence CH$_2$OSO + O must be an extremely powerful methyla"tive agent. In the treatment of methyl chloroformite with SCl$_2$, Glaholm observed the formation of the dimethylchloronium ion on warming. This indicates a very powerful methyla"tive intermediate, which also assumed to be CH$_2$OSO. Hence, if we were to add a nucleophile competitive with SCl$_2$, we could expect the methyla"tion to compete with this catalytic decomposition. This has proven to be the case, and the conversions given in eq 3-6 take place in this system.

$$\text{CH}_2\text{OSO} + \text{HCl} \rightarrow \text{CH}_2\text{O} + \text{SO}_2$$  \hspace{1cm} (3)

$$\text{CH}_2\text{OSO} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{SO} + \text{SO}_2$$  \hspace{1cm} (4)

$$\text{CH}_2\text{OSO} + \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{SO} + \text{SO}_2$$  \hspace{1cm} (5)

$$\text{CH}_2\text{OSO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH} + \text{SO}_2$$  \hspace{1cm} (6)

The identification of these methylated species in solution is based upon proton chemical shifts, occurring at lower field than the parent Compound. The case of dimethyl sulfone, reaction 4, was the least equivocal since the product which is stable and is formed quantitatively, contained two kinds of methyl groups, one at high chemical shift (δ 4.45 (d)) and another one of twice the number of protons at δ 3.63 (d), compared to the starting sulfone (δ 3.65 (s)). The methylation of sulfones, reaction 3, previously reported in a footnote by Jackman is extensible but the product

is short-lived and the ultimate decomposition products have not been identified. The dimethyl sulfate reaction (reaction 5) gave a new peak, δ 4.59 (s), but the conversion was not quantitative. The methyla"tion of this extremely weak nucleophile, better known as a powerful methyla"tive agent itself, is striking. We do not know if the incomplete methyla"lation of dimethyl sulfate results unfavorable equilibrium with MeOSO$_2$ or merely an amount limited kinetically by competition with the weaker nucleophiles present in solution. The methyla"lation of methyl chloroformite, reaction 6, differs from Glaholm's observation only in the counterion present in this system and the deliberate addition of methyl chloride. The methyla"lation of methyl trifluoromethane was not observed.

The identification of the ion MeOSO$_2$ was confirmed by the isolation of its deprotonated reaction product with 2-chloropropene, Peterson's 16 anion reacted with methyl 2-chloro-2-propene sulfinate, identified by proton and 13C NMR, both of which were in essential agreement with the values of Peterson. Electrophilic addition to the double bond will also lead to this product, an attempt to use this ion as a dieneophile, analogous to the reaction 7 reported by Krasnse and Perez did not give an identified low-molecular-weight product with dimethyl-1,3-butadiene.

$$\begin{align*}
\text{CH}_2\text{OSO} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{SO}_2 \\
\text{CH}_2\text{OSO} + \text{CH}_2\text{Cl} & \rightarrow \text{CH}_2\text{OSO} + \text{H}_2\text{O} \\
\text{CH}_2\text{OSO} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{SO}_2 \\
\text{CH}_2\text{OSO} + \text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OSO} + \text{SO}_2 \\
\text{CH}_2\text{OSO} + \text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OSO} + \text{SO}_2 \\
\text{CH}_2\text{OSO} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{SO}_2 \\
\text{CH}_2\text{OSO} + \text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OSO} + \text{SO}_2
\end{align*}$$

Dimethyl sulfoxide is also a potential source of MeOSO$_2$, and this has indeed proven to be a likely fate when it is exposed to powerful methyla"tive agents. We cannot study it in the thionyl chloride–methyl chloroformite–antimony pentachloride system because the sulfone is destroyed by conversion to chlorosulfite by thioryl chloride. Most of the following work is therefore with the milder (but still very powerful) methyl trifluoromethane.

There is no very rapid or conspicuous reaction on treating dimethyl sulfoxide with methyl trifluoromethane. In the NMR a rather small peak at δ 4.5 appears rapidly, but further reactions are very slow. With two parts of CH$_2$OT to one of CH$_2$OSO in CDCl$_3$, there are three peaks immediately visible all singlets. These are δ 3.85 (dimethyl sulfoxide), δ 4.20 (methyl trifluoromethane), and the quite weak singlet δ 4.85, which we attribute to the methylated species, the trimethylsulfonylum ion, (MeOSO)$_2$. This structure is chosen as the one most likely given that only one peak appears. In the course of several weeks, a new peak (singlet) appears at δ 3.60. This is identified as dimethyl ether from its gas chromatographic retention time and the parent peak at δ 4.86. Another new substance in the mass spectrum with m/e 64, not corresponding to any NMR signal, was identified as sulfur dioxide. Thus reaction 4 is

$$\text{CH}_2\text{OSO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH} + \text{SO}_2$$

occurring slowly, although it is not observed at these temperatures with pure dimethyl sulfoxide. After 19 weeks, at room temperature, the dimethyl sulfoxide peak at δ 3.6 had almost disappeared, but the methyl trifluoromethane peak still persisted, virtually unchanged. Thus the methyl trifluoromethane is a catalyst for the decomposition of dimethyl sulfoxide. We postulate the sequence of reactions 9-11.

$$\text{CH}_2\text{OSO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH} + \text{SO}_2$$

$$\text{CH}_2\text{OSO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH} + \text{SO}_2$$

Reaction 10 may correspond to an intramolecular methyl transfer from the trimethylsulfonylum ion to give an unsymmetric (and unseen) isomer (eq 12) followed by its unimolecular cleavage to CH$_2$OSO (eq 13). Alternatively, and kinetically indistinguishable, in addition to the observed reaction 9, there may be an alternative mechanism to give the unobserved isomer cation, reaction 14, followed or occurring simultaneously with the decomposition (eq 13).

Methyl-Transfer Reactions

\[
\begin{align*}
\text{CH}_3\text{O} & \rightarrow \text{CH}_3 \quad \text{(12)} \\
\text{CH}_3\text{O} & \rightarrow \text{CH}_3 \text{O} + \text{CH}_3\text{O} \quad \text{(13)} \\
\text{CH}_3\text{O} & \rightarrow \text{CH}_3 \text{O} + \text{CH}_3\text{O} \quad \text{(14)} \\
\end{align*}
\]

Since the direct methyl transfer (eq 12) has a rather unfavorable geometry for an intramolecular methyl transfer,
we prefer the separate reaction 14 as a more probable source of 1 and consider that reaction 10 as an one-step process is unlikely. The reversible methyl transfer with a much slower rate at the methoxy oxygen is thus a more probable route, with many analogues.
The methyl triflate is catalytic because reactions 10 and 11 (or 12 and 13) constitute an ionic chain. The possible reformulation of methyl triflate from CH₃OSO₂⁺ and OT⁻ is discussed later. The mechanism of reversible alkylolation also accounts for the observation of methoxy-ethyl exchange in the reaction of dimethyl sulfate with methyl triflate, reported recently. The authors of this work, however, did not notice the much slower irreversible decomposition. When dimethyl-sulfate (easily prepared from commercial CD₃OH) is treated with methyl triflate, the NMR shows a relatively rapid exchange, the methyl triflate proton signal disappears, and a strong dimethyl-sulfate signal appears. If an excess of dimethyl sulfate is used, the exchange is almost quantitative, and if the solution is then heated to accelerate the reaction described above, the dimethyl-sulfate undergoes the cationic decomposition to dimethyl ether and sulfur dioxide, leaving CD₃OT almost ununreacted. This constitutes an easier and cheaper synthesis than the route through CH₃⁺ + AgOT⁻ described earlier. This is a practical synthesis of a methyl-d₂ triflate and therefore of a host of other methyl-dₙ compounds, even though much of the deuterium is lost in dimethyl ether, which is observed by GC/MS to contain CH₃OCD₃ as well as CD₃OCD₃ but little undetected material. There are of course other potential syntheses; a referee suggests CD₃OH + T₂O. We searched rather carefully and without success for the two characteristic peaks of methyl methanesulfonate in the 90 MHz instrument. Since the potential S-methylated cation would certainly lose an O-methyl group easily, we conclude that there is no perceptible S-methylation, showing that the rate of S-methylation is far less than that of the reversible O-methylation.

When dimethyl sulfoxide was treated with methyl 2,4,6-trinitrotoluene, the reaction was more complex. In that the powerful methylation agent no longer was catalytic, and it disappeared rather rapidly. The extent of methylation to give trimethoxybenzenesulfonate (4.4.4) was greater, both dimethyl ether and sulfur dioxide were formed, and the disappearance of both methyl and acyl signal in the NMR was hard to understand. The problem was resolved when a precipitate was noted, identified as trimethylbenzenesulfonate methanesulfonic methyl ether (which is present), demonstrating again that it is more powerful in an equilibrium sense than the trimethylbenzequinone ion, and also that this trimethyloxonium salt has a very low solubility (in dimethyl sulfoxide as well as many other solvents).

With both methylation agents we have not been able to tell whether the further reaction 15 is important or not; we are confident that it is thermodynamically favorable with X = OT⁻, but we are not sure with X = SO₂⁻.

\[
\text{MeOSO}⁺ + \text{X} \rightarrow \text{MeX} + \text{SO}_2 \quad \text{(15)}
\]

This reaction with X = OT⁻ would also cause the observed exchange at the methyl groups between sulfite and triflate, but a more quantitative kinetic treatment is required to test this route is necessary as well as the reverse of reaction 9. Reaction 15 would be the termination step in the ionic chain reaction. We have not looked for exchange of the sulfite and trinitrobenzenesulfonate esters.

Experimental Section

Materials. Methyl chlorosulfite was prepared according to published procedures due to Carré and Liberamánchez and Beratésite. It was stored over anhydrous calcium chloride. Dimethyl sulfoxide was prepared from 2 mol of methanol and 1 mol of thionyl chloride.

Commercially available antimony pentachloride was used without purification. Thionyl chloride (MBC) was distilled from triethyl phosphite to obtain a colorless liquid prior to use. Dimethyl-d₂ sulfite was prepared from commercial (Aldrich) CD₃OD and thionyl chloride as a colorless liquid, bp 63 °C (65 mmHg). A solution of SbCl₅ (1.29 M) in thionyl chloride was used. Methyl triflate was stored over molecular sieves in the refrigerator. Sulfones were purified by a procedure described in previous papers.

Proton NMR spectra were recorded from a Varian EM-390 50-MHz instrument. The chemical shifts are with reference to tetramethylsilane (Me₄Si) used as external standard (as a capillary), as well as internal standard. ²³⁷ NMR spectra were recorded on a JEOL FX90Q instrument. GC/MS spectral data were obtained from a Finnigan Series 600 data system.

Methylation Using the CH₃OSO⁺/Cl⁻/SbCl₅/SOCl₂ System. The following procedure for methylation of sulfone is typical of other methylation. To about 0.5 mL of sulfone dissolved in the antimony pentachloride-thionyl chloride solution (1.0 M) at −78 °C was carefully added dropwise methyl chlorosulfite (1.5 mL) with magnetic stirring to keep the vigor of the reaction under control. The mixture was stirred for 15 min at this temperature and then slowly allowed to warm. Addition of an antimony pentachloride solution in thionyl chloride to a sulfone in methyl chlorosulfite gave similar results. NMR samples were taken when the temperature reached −30 °C, but further warming to ca. 20 °C occurred before the spectra were complete.

The chemical shifts with external Me₄Si reference are as follows: sulfones, δ 3.2 (br t, 2H), 5.6 (br t, 2H), after methylation. Methoxy protons δ 4.3 (t, 1H), δ 4.1 (br t, 1H), δ 5.0 (br t); dimethyl sulfoxide, δ 4.0 (t, 2H), after methylation δ 3.8 (t, 2H, δ 2.9 (br t); dimethyl sulfite, δ 3.9 (t, 1H), after methylation δ 4.3 (t, 1H, δ 4.3 (br t)) dimethyl sulfoxide δ 3.4 (t, 1H, after methylation δ 4.6 (s, methyl chloride after methylation). δ 5.0 (s, intensity increase at cost of CH₂Cl signal) when more of the methyl chlorosulfite is added. The CH₂Cl-SO₂Cl peak at δ 5.9 was observed here as well as in some other cases. No new peaks were observed in the system containing methyl triflate as a "methylator".

Detection of CH₂OSOCl by the Ems Reaction. The procedure is based on that of Peterson. ² Chloroperoxybenzoic (1.5 g) and methyl chlorosulfite (5.7 g) were cooled to −78 °C in a round-bottomed flask. A solution of antimony pentachloride (6.0 g) in dichloromethane (12 mL) cooled to −78 °C was slowly added with stirring. The system was well-mixed and then immediately poured into a solution of methanol (10 mL) containing sodium bicarbonate (0.5 g) cooled to −60 °C. After the solution was stirred and warmed to room temperature, the workup followed that of Peterson, giving a pale-yellow oil with the following:¹² NMR in CDCl₃, with internal Me₄Si: δ 3.74 (s, a methoxy (3.75), 3.60 (d, CH₃S) (3.65), 5.43 (s, =CH₂) (5.48). Values in parentheses are from ref 6. The ¹³C spectrum in DCCl₃ gave 65.65 (83.6) (CH₂O), 65.98 (86.2) (CH₃S), 118.67 (131.6) (=CH₃), 129.68 (131.6) (=CCl). The discrepancies in the ¹³C chemical shifts are not serious and the multiplicities on off-resonance decoupling were appropriate for the structure CH₂OSO/CH₃CCl=CH₂. The "doublet" reported for the CH₂S peak is probably not a coupling but represents


121. \[\text{(19) Beraté, G. J. Am. Chem. Soc. 1951, 73, 121.} \]

1957. \[\text{(20) Ems, L. F.; Fickert, M. "Benzil and its Synthetic Syntheses." Wiley-} \]
a chemical shift difference of the diastereotopic protons.

Reactions of Dimethyl Sulfite with Methyl Triflate. These reactions were mostly done in NMR tubes, and the products were identified by proton chemical shifts and volatile products by GC/MS. In addition to dimethyl sulfite, methyl triflate, and dimethyl ether, a small peak identified as the trimethyloxonium ion, expected from dimethyl ether and methyl triflate, was also sometimes observed. The peaks for methyl methanesulfonate, especially those of the sulfur-bound methyl, are well-resolved from any others and were not detectable in this system.

Reaction of Dimethyl Sulfite and Methyl 2,4,6-Trinitrobenzenesulfonate. With excess dimethyl sulfite, dimethyl ether and sulfur dioxide were detected by GC/MS, the peaks of the methylating agent disappeared, and a solid was formed, identified by its melting point as trimethyloxonium 2,4,6-trinitrobenzenesulfonate, mp 181 °C.

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Registry No. CH$_3$OSO$_2$Cl, 13185-72-4; dimethyl sulfite, 619-43-2; methyl triflate, 333-27-7; methyl 2,4,6-trinitrobenzenesulfonate, 55541-31-4; methyl chloride, 74-97-3; dimethylsulfate, 77-78-1; sulfolane, 156-29-5; dimethyl sulfone, 87-71-3.
Appendix III

Synthesis of Constituents of the Boll Weevil Sex Attractant
Synthesis of Constituents of the Boll Weevil Sex Attractant


Department of Chemistry, Rice University,
P.O. Box 1892, Houston, Texas 77251, U.S.A.

The utilization of the boll weevil sex attractant, compounds 1–4, as part of a multidisciplinary technology to eradicate this insect has placed the synthesis of these compounds into a strategic position with regard to procurement.\textsuperscript{1,2} We report here a convenient procedure which we have used to prepare the aldehydes 2 and 3 (Scheme I).\textsuperscript{3}

Using commercially available 5,5-dimethylcyclohexane-1,3-dione (5, dimedone) as a point of departure, 3-chloro-5,5-dimethylcyclohex-2-en-1-one (6) was synthesized as described by Clark and Heathcock\textsuperscript{4} and converted to 3,3-dimethylcyclohexanone (7) by reduction over 10% Pd/C
Scheme I

5 + (COCl)₂ → CHCl₃ → 6 + H₂, Pd/C → benzene

7 + LiC₆H₄-H₂NCH₂CH₂NH₂ → benzene/THF → 8

(Ph₃SiO)₃VO → PhCO₂H → mineral oil → 2 + 3 +

9 + 10
in benzene.\textsuperscript{5} The discovery by Cormier\textsuperscript{6} that dimedone can be reduced directly to 3,3-dimethylcyclohexanone over Pd/charcoal makes this material readily and cheaply available. Treatment of \textsuperscript{7} with 1.5 equiv of lithium acetylide-ethylenediamine complex in benzene/tetrahydrofuran afforded 1-ethynyl-3,3-dimethylcyclohexanol (8) in 75\% yield.\textsuperscript{3d} The acetylenic alcohol was converted in 79\% yield to the desired aldehydes \textsuperscript{2} and \textsuperscript{3} (ratio 51:49, respectively)\textsuperscript{7} along with ca. 18\% of \textsuperscript{9} and \textsuperscript{10} by heating a mixture of \textsuperscript{8}, 10 mole percent of tris(triphenylsilyl)vanadate(V), triphenylsilanol and 0.7 mole percent benzoic acid in mineral oil for 4 hr at 140$^\circ$C.\textsuperscript{8} The aldehydes were then isolated by vacuum distillation.

\textbf{Experimental}

Proton magnetic resonance spectra were recorded at 90 MHz using a Varian Model EM-390 spectrometer. Infrared spectra were recorded on a Beckman IR 4230 spectrometer. A Finnigan Model 3300 gas chromatograph-mass spectrometer equipped with a 4 ft x 1/8 in. nickel column packed with 5\% SE-30 on Chromosorb G was used to obtain mass spectra. A Hewlett-Packard Model 700 gas chromatograph equipped with a 6 ft x 1/4 in. column packed with 10\% FFAP on Chromosorb WAW was used for analytical gas chromatography. Boiling points are uncorrected.
5,5-Dimethylcyclohexane-1,3-dione (dimedone), oxalyl chloride, lithium acetylide-ethylene diamine complex and triphenylsilanol were obtained from Aldrich Chemical Company, Inc. Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. Benzene was distilled from calcium hydride and stored over 4A molecular sieves. Alcohol free chloroform was used.

**Preparation of 3,3-Dimethylcyclohexanone (7).** A solution of 6 (10.78 g, 67.96 mmol) in benzene (200 mL) was reduced over 10% Pd/C at 3 atm using a Parr hydrogenation apparatus. Hydrogen chloride was vented periodically. After hydrogen uptake ceased (ca. 8 hr), the mixture was filtered, washed with saturated aqueous NaHCO₃, dried over MgSO₄, and most of the solvent removed at 1 atm. Distillation of the residue provided 7.40 g (77.5% yield from dimedone) of 7, bp 63-64/12 mm (lit. ³d 58-60/15 mm Hg). The yield of 7 obtained from the reduction of 6 is 99%.

**Preparation of 1-Ethynyl-3,3-dimethylcyclohexanol (8).** The procedure of Pelletier and Mody was used.³d Thus a solution of 7 (3.86 g, 31 mmol) in benzene/tetrahydrofuran (10 mL, 50:50) was added dropwise under nitrogen at 35⁰C to a slurry of lithium acetylide-ethylenediamine complex (5.2 g, 57 mmol) in benzene/tetrahydrofuran (50 mL) and stirred for 4 hr at room temperature. Water (50 mL) was then added and the mixture refluxed for 15 min. The organic layer was separated, dried over MgSO₄ and concentrated in vacuo. Distillation provided 3.45 g (73% yield) of 8.
bp 58-59°C/1.5 mm Hg.

Rearrangement of 1-Ethynyl-3,3-dimethylcyclohexanol (8). A mixture of tris(triphenylsilyl)vanadate(V) (293 mg, 0.328 mmol), triphenylsilanol (136 mg, 0.492 mmol), benzoic acid (28 mg, 0.229 mmol), mineral oil (15 mL), and 1-ethynyl-3,3-dimethylcyclohexanol (508 mg, 3.34 mmol) was heated for 3.5 hr at 140°C. The mixture was then cooled to 90°C and the volatile products (576.8 mg) were removed by distillation at 0.05 mm Hg. After drying, the distilled product was shown by GC to be 79% 2 and 3 (ratio 51:49), 18% 9 and 10 and 2% of unreacted 8. The structures of 2 and 3 were confirmed by comparing spectral properties (IR, NMR, MS) with those reported. Compounds 9 and 10 were shown by mass spectrometry to be isomers of 2 and 3. Compound 9 exhibits NMR signals at 0.95 (t, J = 3 Hz, 1 H) and 5.27 (narrow m, 1 H). Aldehyde 10 has signals at 0.95 (t, J = 3 Hz, 1 H) and 5.5 (broad m, 1 H).

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References and Notes


7. The ratio was determined by integration (NMR) of the aldehydeic protons.