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I. GENERATION OF METHYLENECYCLOPROPENE. II.
ATTEMPTED SYNTHESIS OF
ANTHRO(B)CYCLOPROPENE.

RICE UNIVERSITY, PH.D., 1978

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I. GENERATION OF METHYLENECYCLOPROPENE
II. ATTEMPTED SYNTHESIS OF ANTHRO[b]CYCLOPROPENE

by

MEHMET YILMAZ ASIM

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

DOCTOR OF PHILOSOPHY

THESIS DIRECTOR'S SIGNATURE:

W. E. Billups

HOUSTON, TEXAS
May, 1978
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To My Beloved Mother
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PART I. GENERATION OF METHYLENECYCLOPROPENE
INTRODUCTION

Chemists have long been fascinated by strained small ring systems and, in particular, the C₄H₄ family has aroused the interest of theoreticians, as well as providing a synthetic challenge. An important member of this group of hydrocarbons is methylenecyclopropene, ¹, which, although inferred recently from trapping experiments, ² is unknown as a stable entity. Other prominent members of the C₄H₄ family are cyclobutadiene, ², which has been detected convincingly as a short-lived species, ³ and tetrahedrane, ³, which has been suggested as a reactive intermediate. ⁵

As the simplest cross-conjugated cyclic system, methylenecyclopropene is also of interest because of its relationship to 1-methylenecycloheptatriene (heptafulvene), ⁴, and cyclopropenone, ⁵ ⁶ ⁷ The latter are marvels of stability by virtue of stabilization derived from resonance with the aromatic dipole.
Although molecular orbital calculations on suggest that it possesses minor resonance stabilization, the high index of free valency at the exocyclic methylene group is expected to lead to polymerization, a process which also relieves strain. Dewar and his co-workers have calculated the strain energy of 1 to be 58.1 kcal/mole and the heat of formation to be 79.1 kcal/mole.

Equation 1 shows an early attempt to synthesize this highly elusive hydrocarbon. Thus photolysis and flash vacuum pyrolysis of cis-1-methylene-2,3-dicarboxylic anhydride, did not afford methylenecyclopropene, but, instead, vinlylacetylene.

* For a definition of the free-valence index, see e.g. A. Streitwieser, Jr., Molecular Orbital Theory, Wiley New York - London, 1961, p.56
and small amounts of acetylene and methylacetylene. A base-induced elimination-isomerization approach (Equation 2) employed by Shields and Gardner using 1,1-dichloro-2-methylcyclopropane as the precursor produced only polymer.

\[ \text{CH}_3 \quad \text{Cl} \quad \longrightarrow \quad \text{CH}_3 \quad \text{Cl} \quad \longrightarrow \quad \text{Cl} \quad \longrightarrow \quad \text{1} \]

\[ \text{CH}_3 \quad \text{Cl} \quad \longrightarrow \quad \text{Polymer} \]

Equation 2

Stabilization of the methylenecyclopropene system can be expected if (i) the C4-atom is made part of a system delocalizing the negative charge, or if (ii) the three-membered ring is incorporated into a system delocalizing the positive charge. Utilizing this concept, four types of resonance-stabilized methylenecyclopropenes have heretofore been synthesized and studied:

(1) methylenecyclopropenes, \( \text{I} \), with the C4-atom bearing electron-withdrawing substituents such as CN, COOR, COR, etc.
(2) methylenecyclopropanes, 8, whereby the C₄-atom is incorporated into a cyclopentadienyl system.

(3) methylenecyclopropanes, 9, which have the C₄-atom as part of a quinomethane (X = 0) or quinodimethane (X = CR₂) system.

(4) methylenecyclopropanes, 10, cyclopropenium cyanines which combine the three-membered ring with another donor group.

\[ 9_{a}: X=0 \]
\[ 9_{b}: X=CR \]
\[ R' \]

There are some methylenecyclopropanes whose stability is derived from inductive effects brought about by strongly electron-withdrawing substituents. Therefore, 1,2-bis-(p-tolyl)-4,4-(bis-trifluoromethyl)methylene-
11, recently synthesized by Agranat, is a very stable molecule with a dipole moment (7.42D) comparable to that of 1,2-diphenyl-4,4-dicyanomethylenecyclopropene, 12, (7.9D).

Likewise, methylenecyclopropenes, 13 and 14, substituted by fluorine have been synthesized and are stable.

\[ \begin{align*}
\text{p-tolyl} & \quad \text{p-tolyl} \\
F_3C & \quad CF_3 \\
\text{Ph} & \quad \text{Ph} \\
NC & \quad CN \\
\text{11} & \quad \text{12} \\
\text{CF}_3 & \quad \text{CF}_3 \\
F & \quad F \\
\text{F} & \quad \text{CF}_3 \\
\text{13} & \quad \text{14}
\end{align*} \]

The methylenecyclopropenes discussed above have all utilized the electronic stability such that they all have strongly electron-withdrawing substituents on the C4-atom. Very recently some methylenecyclopropenes with t-butyl substituents used as appropriate shielding groups have been synthesized and shown to be isolable. This approach which employed stability from steric shielding was undertaken by A. J. Blakeney in our laboratory. The following methylenecyclopropenes were reported.

\[ \begin{align*}
\text{Br} & \quad \text{t-Bu} \\
\text{H} & \quad \text{t-Bu} \\
\text{15} & \quad \text{16} \\
\text{Br} & \quad \text{t-Bu} \\
\text{t-Bu} & \quad \text{H}
\end{align*} \]

Special precautions had to be taken because 15 as well as 16 proved to be highly reactive with H2O and unstable in
solution above 0°.\textsuperscript{24}

Synthesis of Methylene cyclopropanes:

One of the first syntheses of methylene cyclopropanes employed the Wittig reaction of diphenyl cyclopropenone with triphenyl carbomethoxymethylene phosphorane, yielding 18 (Equation 3).\textsuperscript{25} This method, however, did not prove to be a general one.

The inverse functionalization of the components for a Wittig reaction was reported by Semenov and co-workers\textsuperscript{26}, where the cyclopropenylide, 19, was reacted with aldehydes to afford the unstable methylene cyclopropanes 20 identified by protonation as cyclopropenium salts 21, (Equation 4).
Methylenecyclopropene, 18, was also synthesized by a different route using diphenyl cyclopropenium cation and lithio ethyl acetate (Equation 5).\textsuperscript{27}  

\[ \text{Ph} \quad \text{Ph} \quad \overset{\ominus}{\text{LiCH}_2\text{CO}_2\text{Et}} \quad \overset{\ominus}{\text{Ph}} \quad \overset{-\text{H}^\ominus}{\text{CH}_2\text{CO}_2\text{Et}} \quad \overset{\text{Ph}_3\text{C}^\ominus}{\text{Ph}} \quad \overset{\text{Base}}{-\text{H}^\ominus} \quad \overset{\ominus}{\text{CH}_2\text{CO}_2\text{Et}} \quad \overset{18}{\sim} \]  

This route found wide usage in the synthesis of calicene derivatives (Equation 6).\textsuperscript{28-32} However, it did not prove to be of general application in methylenecyclopropene synthesis.

\[ \text{Ph} \quad \overset{\ominus}{\text{H}} \quad \overset{\ominus}{\text{Ph}} \quad \overset{\text{H}}{\text{Li}} \quad \overset{\text{CH}_2\text{CO}_2\text{Et}}{\rightarrow} \quad \overset{\text{Ph}}{\text{H}} \quad \overset{\text{Ph}}{\overset{-\text{H}^\ominus}{\text{H}}} \quad \overset{\text{Ph}}{\overset{-\text{H}^\ominus}{\text{Ph}}} \]  

A widely used and general method is the classical condensation of suitable reactive methylene compounds (such as malononitrile or cyanoacetate) with cyclopropenones (Equation 7).\textsuperscript{33,34}  

\[ \overset{\text{R, R''}}{\text{R'}} \quad \overset{\text{CN}}{\text{CH}_2\text{CN}} \quad \overset{\overset{\text{R'}}{\text{R}}}{\text{Ac}_2\text{O}, \text{-H}_2\text{O}} \quad \overset{\text{CN}}{\text{R'}} \quad \overset{\text{CN}}{\text{R''}} \quad \overset{\text{CN}}{\text{R''}} \]  

\(\text{R, R''}= \text{aryl, alkyl} \)  
\(\text{R'}= \text{CN, CO}_2\text{R}\)
The use of alkoxy cyclopropenium cations (Equation 8) further expands the scope of this synthesis. The alkoxy cyclopropenium cations can be readily prepared by alkylation of cyclopropanones with trialkyloxonium tetrafluoroborates.

When 3-ethoxy-diphenyl cyclopropenium cation, 22, was reacted with methylene compounds X-CH2-Y (X,Y = CN, COOR, COR, p-nitro-phenyl, etc.) and a tertiary non-nucleophilic base, di-isopropylethylamine (DIPEA), a very high yield of methylene-cyclopropene was obtained.

When 22 was reacted with 1,3-dicarbonyl compounds, no methylenecyclopropene was formed. Reaction of the cation 23 with a copper or zinc chelate 24 of 1,3-dicarbonyl compounds (Equation 9) affords a very high yield of the corresponding 4,4-diacyl methylenecyclopropene, 25.
Special cases involving preparations of methylenecyclopropenes were found in the base-induced reaction of the nitroso compound \( \sim \) with dimethyl fumarate \(^4\) (Equation 10), in the thermolysis of tetrafluorocyclopropene reported to give the perfluorinated methylenecyclopropenes \( \sim \) and \( \sim \),\(^{22}\) and in the addition of bis(trifluoromethyl)ketene to bis-(p-tolyl)cyclopropenone,\(^{20}\) which gave rise to methylenecyclopropene \( \sim \) by elimination of \( \text{CO}_2 \) (Equation 11).

The first synthesis of a stable methylenecyclopropene, namely 1,2-diphenyl-3,4'-(2',6'-dibromoquinol)cyclopropene,
29, was successfully achieved in 1964 by Kende. The thermal cleavage of the ether linkage in the cyclopropenylum salt, 28, was followed by bromination of the resulting diphenyl-\((p\)-hydroxyphenyl\)cyclopropenium bromide with N-bromosuccinimide and finally by reversible elimination of HBr with a tertiary amine to yield 29 (Equation 12):

![Chemical structure diagram](image)

\[(12)\]

28

This synthesis proved to be very general for quinocyclopropenes of structure 9a. The needed \(p\)-hydroxy-phenyl cyclopropenium cations are easily synthesized by electrophilic substitution of phenolic compounds (preferably 2,6-disubstituted) with heterosubstituted cyclopropenium cations, 22 and 30. A representative example is provided below in Equation 13:

![Chemical structure diagram](image)

\[(13)\]

\[
X = \text{Cl} : 30, \quad X = \text{OBt} : 22
\]

\[= \text{C(CH}_3\text{)}_3\]
The cyclopropenium cyanines of Type 10 may be synthesized by reacting the cyclopropenium systems with a large number of donor groups, mainly heterocyclic and carbocyclic systems.

Enamines, ketene acetals and 2- or 4-alkylsubstituted heterocyclic quarternary salts of pyridine, quinoline, and benzothiazol may be "cyclopropenylated" with the ethoxy cyclopropenium cation, 22. 35, 44

The electrophilic attack of cation 22 at the five-membered ring of azulene 45 and 4,6,8-trimethyl azulene 46 leads to 1-(1', 2'-diphenyl-cyclopropenium)azulenes, 30 (Equation 15).
### TABLE I

**PREPARATION OF SOME METHYLENECYCLOPROPENES OF TYPE 7**

<table>
<thead>
<tr>
<th>Methylenecyclopropene</th>
<th>Yield (%)</th>
<th>Method</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = CH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R' = R'' = CN</td>
<td>41</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R' = CN, R'' = COOCH₃</td>
<td>34</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R' = R'' = COOCH₃</td>
<td>22</td>
<td>Cu-chelate</td>
<td>7</td>
</tr>
<tr>
<td>R' = R'' = dimedone</td>
<td>58</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R' = CN, R'' = NO₂</td>
<td>43</td>
<td>NH₄ salt of</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NC-CH₂-NO₂</td>
<td></td>
</tr>
<tr>
<td>R' = CN, R'' = COC₆H₅</td>
<td>35</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R' = CN, R'' = P-NO₂-C₆H₄</td>
<td>8</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R = n-C₃H₇</td>
<td>18</td>
<td>Acetic anhydride</td>
<td>34</td>
</tr>
<tr>
<td>R' = R'' = CN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = -(C₂H₂)₅⁻</td>
<td>58</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R' = R'' = CN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar = C₆H₅</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R' = R'' = CN</td>
<td>85</td>
<td>DIPEA</td>
<td>37</td>
</tr>
<tr>
<td>R' = CN, R'' = COOCH₃</td>
<td>82</td>
<td>DIPEA</td>
<td>37</td>
</tr>
<tr>
<td>R' = CN, R'' = COOC₂H₅</td>
<td>70</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>Acetic anhydride</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ alanine</td>
<td></td>
</tr>
<tr>
<td>Methylenecyclopropene</td>
<td>Yield (%)</td>
<td>Method</td>
<td>Refs.</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------</td>
<td>--------------</td>
<td>-------</td>
</tr>
<tr>
<td>$R' = CN, R'' = COC_6H_5$</td>
<td>66</td>
<td>DIPEA</td>
<td>47</td>
</tr>
<tr>
<td>$R' = R'' = COCH_3$</td>
<td>80</td>
<td>Cu-chelate</td>
<td>39</td>
</tr>
<tr>
<td>$R' = R'' = COC_6H_5$</td>
<td>80</td>
<td>Cu-chelate</td>
<td>7</td>
</tr>
<tr>
<td>$R' = COC_6H_5, R'' = CO_2C_2H_5$</td>
<td>62</td>
<td>Cu-chelate</td>
<td>39</td>
</tr>
<tr>
<td>$R' = COCH_3, R'' = CONHC_6H_5$</td>
<td>78</td>
<td>Cu-chelate</td>
<td>39</td>
</tr>
<tr>
<td>$R' = COC_6H_5, R'' = CHO$</td>
<td>74</td>
<td>Cu-chelate</td>
<td>39</td>
</tr>
<tr>
<td>$R' = R'' = dimedone$</td>
<td>64</td>
<td>DIPEA</td>
<td>37</td>
</tr>
<tr>
<td>$R' = R'' = meldrum acid$</td>
<td>53</td>
<td>DIPEA</td>
<td>37</td>
</tr>
<tr>
<td>$R' = R'' = indane dione$</td>
<td>64</td>
<td>Acetic anhydride</td>
<td></td>
</tr>
<tr>
<td>$R' = H, R'' = -CPh=C(CN)_2$</td>
<td>24</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>$R' = COOC_2H_5$</td>
<td>95</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>$R'' = -C=C(CN)_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CH_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R' = CN, R'' = NO_2$</td>
<td>61</td>
<td>NH$_4$-salt of</td>
<td>7</td>
</tr>
<tr>
<td>$Ar = p-CH_3-C_6H_4$</td>
<td>59</td>
<td>bis-p-tolylcyclo-</td>
<td>20</td>
</tr>
<tr>
<td>$R' = R'' = CF_3$</td>
<td></td>
<td>propene +</td>
<td></td>
</tr>
<tr>
<td>$R = CH_3$</td>
<td></td>
<td>(CF$_3$)$_2$C=C=O</td>
<td></td>
</tr>
<tr>
<td>$R' = R'' = COCH_3$</td>
<td>74</td>
<td>Cu-chelate</td>
<td>49</td>
</tr>
<tr>
<td>$R' = COCH_3, R'' = CONHC_6H_5$</td>
<td>96</td>
<td>Cu-chelate</td>
<td>49</td>
</tr>
<tr>
<td>$R' = CN, R'' = NO_2$</td>
<td>96</td>
<td>NH$_4$-salt of</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NC-$CH_2$-NO$_2$</td>
<td></td>
</tr>
<tr>
<td>Methylenecyclopropene</td>
<td>Yield (%)</td>
<td>Method</td>
<td>Refs.</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>R'=R''=CN</td>
<td>19</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R'=R''=dimedone</td>
<td>65</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R=C(CH₃)₃</td>
<td>27</td>
<td>DIPEA</td>
<td>7</td>
</tr>
<tr>
<td>R'=R''=CN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R'=R''=COCH₃</td>
<td>16</td>
<td>Cu-chelate</td>
<td>7</td>
</tr>
<tr>
<td>R'=COCH₃, R''=COC₆H₅</td>
<td>27</td>
<td>Without base</td>
<td>7</td>
</tr>
</tbody>
</table>
Stang reported the ready in situ preparation under mild conditions of simple alkyl methylenecyclopropenes. This synthesis involves the addition of vinylcarbenes to acetylenes (Equation 16). When an appropriate vinyl triflate is treated

![Chemical structure](image)

(16)

with a strong base, the vinylcarbene is generated via α-elimination, and it adds to the multiple bond of the acetylene.

The scope of this synthesis is limited to cases where R and R' are not H, and cases where \( R^2 \) and \( R^3 \) are not aryl. As of this writing, the only examples reported and synthesized are those wherein \( R'=R=\text{Me} \) and \( R^2=3^2=\text{CH}_3 \) or \( \text{CH}_2\text{CH}_3 \). Although isolation of these compounds met with no success, the corresponding crystalline cycloproponium perchlorate salts as well as the Diels-Alder trapping adducts with cyclopentadiene have been obtained and characterized.

With the exception of Stang's synthesis, all the methylenecyclopropenes discussed above derive their stability from electronic stabilization. Very recently in our laboratory Blakeney employed an alternate concept of stabilization by steric protection,¹⁴ (see page 5). Precedent for steric protection of labile compounds is found in earlier work which describes the stabilization of cyclobutadiene and cyclopropanone by the incorporation of \( \text{t-butyl} \) groups.⁵¹-⁵⁴
Blakeney's synthesis, as depicted in Equation 17, involved the addition of dibromocarbene to 1,3-di-t-butylallene, yielding the adduct 32 which is favored because of the approach of the bulky carbene from the less hindered side of 31. Acid-equilibration then favored the least sterically crowded isomer 33.

\[
\begin{align*}
\text{31} & \xrightarrow{\text{:CBr}_2} 32 & 33 \\
& \xrightarrow{\text{HBr}} & \\
\text{32} & \xrightarrow{\text{KOT-Bu}} \text{THF} \quad -40^\circ & \text{15} & \xrightarrow{\text{KOT-Bu}} \text{THF} \quad -40^\circ \\
& & \text{16} \\
\end{align*}
\]

Elimination of HBr from 32 and 33 with strong base (KOT-Bu) at -40° afforded the 1,4-di-t-butylmethylenecyclopropenes, 15 and 16, respectively. Special precautions had to be employed since 15 (as well as 16) reacted vigorously with H₂O and were unstable in solution above 0°. Instead of the usual work-up procedure
the reaction mixtures were filtered through a special apparatus (see Blakeney's thesis), THF and t-BuOH pumped off and cooled CCl₄ added. Repetition of this process 8 times yielded cooled CCl₄ solutions of 15 and 16 from which spectral data were obtained.

Attention was then focused upon the synthesis of the parent methylenecyclopropene, 1. Once again, our group undertook an approach which involved addition of chloromethylcarbene, generated in situ by the method of Olah to vinyl chloride, to

\[
\text{CH}_3\text{CHCl}_2 \xrightarrow{n-\text{BuLi}} \text{Et}_2\text{O} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
34 \\
\sim
\end{array}
\]

(18)

give a 5% yield of the 1,2-dichloro-1-methylenecyclopropane, 34. (Equation 18).

The disadvantages of this synthesis were twofold; the very low yield and the purification of the product which could only be achieved by preparative glpc. Nevertheless, it offered a reasonable and viable approach to 1. Reaction of 34 with KOT-Bu afforded 2-t-butoxymethylene cyclopropane, 35 (Equation 19).

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{Ot- Bu}
\end{array}
\]

\[
\begin{array}{c}
34 \\
\sim
\end{array} \rightarrow \begin{array}{c}
35 \\
\sim
\end{array}
\]

(19)
The formation of \( \sim \) was rationalized in terms of \( \sim \) as a reactive intermediate, although other paths which bypass methylenecyclopropene in forming \( \sim \) were not rigorously excluded.

Much more convincing evidence for the intermediacy of methylenecyclopropene is provided in Equation 20. Reaction of \( 34 \) with KOT-Bu in the presence of CH$_3$S$^\ominus$ gave \( 36 \).

\[
\begin{array}{ccc}
34 & \xrightarrow{\text{KOT-Bu}} & \xrightarrow{\text{H$_2$O$_2$}} \xrightarrow{\text{AcOH}} \xrightarrow{\text{KOT-Bu}} 35 \\
\text{CH}_3S^\ominus & & \text{H$_2$O$_2$} \\
& & \text{AcOH} \\
& & \text{SO}_2\text{CH}_3 \\
36 & 37 & \sim \\
\end{array}
\]

Oxidation of \( 36 \) produced the sulfone \( 37 \). When \( \sim \) was treated with KOT-Bu, \( 35 \) was obtained as the only product.

Since \( \beta \)-elimination of sulfones to give alkenes are well known\textsuperscript{56}, these results afford the most compelling evidence for the intermediacy of methylenecyclopropene.
Structural Criteria of Methylenecyclopropanes:

As shown in Table II high dipole moments are very characteristic of methylenecyclopropanes.

**TABLE II**

**DIPOLE MOMENTS OF SOME METHYLENECYCLOPROPENES**

(given in D)

\[
\begin{align*}
\text{Ar} &= p\text{-tolyl, } R = R' = \text{CF}_3 & 7.42^{20} \\
\text{Ar} &= \text{phenyl, } R = R' = \text{CN} & 7.90^{21} \\
\text{Ar} &= \text{phenyl, } R = \text{CN} & 5.90^{21} \\
R' &= \text{COOC}_2\text{H}_5
\end{align*}
\]

\[
\begin{align*}
9.4^{43} & & 6.3^{57} & & 14.3^{58} & & R = n\text{-C}_3\text{H}_7 & 7.56^{59} \\
& & & & & R = \text{Ph} & 7.97^{60}
\end{align*}
\]
The molecular structures of 1,2-dimethyl-4,4-dicyano methylenecyclopropene, 1,2-diphenyl-4,4-dicyano methylenecyclopropene, 1,2-di-(p-toly)-4,4-di-(trifluoromethyl)-methylenecyclopropene, 5,6-diphenyl, and 5,6-di-n-propyl 1,2,3,4-tetrachlorocalicene and 8-cyano-8-(di-phenylcyclopropenyl)-heptafulvenylium tetrafluoroborate have been obtained by x-ray analysis.

\[
\begin{align*}
R = \text{CH}_3 & : 38 & R = \text{n-C}_3\text{H}_7 & : 38 & R = \text{Ph} & : 39 \\
R = \text{Ph} & : 12 & R = \text{Ph} & : 40
\end{align*}
\]

The relevant parameters of this three-membered system are tabulated in Table III.
From these results, the following conclusions are made:

(a) The $C^3-C^{1(2)}$ distances in the substituted methylene-cyclopropenes do not vary markedly (as a reference the C=C 1.30 Å $^{65}$ in cyclopropene is used).

(b) The average of $C^1-C^2$ and $C^3-C^{1(2)}$ distances in all cases comes close to the 1.373 Å three-membered ring length in triphenyl cyclopropenium perchlorate $^{66}$ and the 1.363 Å distance in tris(dimethylamino) cyclopropenium perchlorate. $^{67}$ Also, the $C^{1(2)}$-phenyl bonds are in very good agreement with triphenyl cyclopropenium cation (average 1.436 Å) and are shorter than the usual C(sp$^2$)-C(sp$^2$) bond distance of 1.480 Å. $^{68}$

(c) The small differences between C-C and C=C bond lengths in the above methylene-cyclopropene indicate some "cyclopropenium" character.

The structural parameters were used in CNDO/2 calculations giving knowledge on charge separation in 38. A high (+) charge was assigned to the centers $C^1/C^2$. This is confirmed by the reactivity of the methylene-cyclopropene, 38, towards nucleophiles (as will be seen later), which attacks at $C^1/C^2$ carbons.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\frac{1}{C=\alpha} \frac{2}{C}$</th>
<th>$\frac{3}{C=\beta} - \frac{1(2)}{C}$ (average)</th>
<th>$\frac{3}{C=\gamma}$</th>
<th>$\frac{4}{C=\alpha}$</th>
<th>$\frac{1(2)}{C}$-Ph $\frac{\phi}{\phi}$ (average)</th>
<th>$\chi_\phi$</th>
<th>$\chi_\gamma$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Diphenyl-4,4-dicyanomethylene-cyclopropene (12)</td>
<td>1.344</td>
<td>1.398</td>
<td>1.367</td>
<td>1.444</td>
<td>61.3</td>
<td>151.3</td>
<td>57.5</td>
<td>61</td>
</tr>
<tr>
<td>1,2-Dimethyl-4,4-dicyanomethylene-cyclopropene (38)</td>
<td>1.327</td>
<td>1.393</td>
<td>1.367</td>
<td>-</td>
<td>61.6</td>
<td>-</td>
<td>56.9</td>
<td>7</td>
</tr>
<tr>
<td>1,2-Di(p-tolyl)-4,4-di-(trifluoromethyl)-methylenecyclopropene (11)</td>
<td>1.342</td>
<td>1.417</td>
<td>1.357</td>
<td>1.445</td>
<td>61.7</td>
<td>149.0</td>
<td>56.5</td>
<td>7</td>
</tr>
<tr>
<td>5,6-Diphenyl-tetrachlorocalicene (39)</td>
<td>1.349</td>
<td>1.413</td>
<td>1.357</td>
<td>1.433</td>
<td>61.5</td>
<td>146.3</td>
<td>57.0</td>
<td>62</td>
</tr>
<tr>
<td>5,6-Di-n-propyl-tetrachlorocalicene (38)</td>
<td>1.320</td>
<td>1.390</td>
<td>1.370</td>
<td>-</td>
<td>61.7</td>
<td>151.0</td>
<td>56.7</td>
<td>63</td>
</tr>
<tr>
<td>Heptafulvenylum cation (40)</td>
<td>1.353</td>
<td>1.400</td>
<td>1.380</td>
<td>1.431</td>
<td>60.9</td>
<td>-</td>
<td>61.3</td>
<td>64</td>
</tr>
</tbody>
</table>
Figure 1 shows the MO scheme as well as the bond orders and free valencies of methylenecyclopropene.

MO - energy (β)

\[ \begin{align*}
\text{Symmetry} & \quad \text{C}_{2v} \\
\beta & \quad -1.481 (B_1) \\
\beta & \quad -1.000 (A_1) \\
\beta & \quad +0.311 (B_1) \\
2\beta & \quad +2.170 (B_1)
\end{align*} \]

bond orders: \[ \begin{align*}
c^1 - c^2 & : 0.818 \\
c^{1(2)} - c^3 & : 0.453 \\
c^3 - c^4 & : 0.758
\end{align*} \]

free valencies: \[ \begin{align*}
c^{1(2)} & : 0.462 \\
c^3 & : 0.068 \\
c^4 & : 0.974
\end{align*} \]

\[ \text{total } \pi - \text{electron density} = 4.962 \]
Spectroscopic Properties of Methylene cyclopropanes:

Two characteristic bands are displayed in the infrared spectra of methylene cyclopropanes, one in the region of 1810-1880 cm\(^{-1}\) and the other between 1510 and 1550 cm\(^{-1}\) as shown by the following examples of alkyl-substituted methylene cyclopropanes.\(^7,16,25,33,34\)

For Comparison:

\[
\begin{array}{ccc}
\text{CH}_3 & \text{CH}_3 & \text{H}_{\text{C}_2}\text{H}_7 \\
\text{CN} & \text{CN} & \text{CN} \\
1870 & 1879 & 1890 \\
1510 & 1579 & 1552
\end{array}
\]

\[
\begin{array}{ccc}
\text{CH}_3 & \text{CH}_3 & \text{CO}_2\text{CH}_3 \\
\text{CN} & \text{NC} & \text{CO}_2\text{Ph} \\
1870 & 1865 & 1680 (C=O) \\
1515 & 1515 & 1610 (C=O)
\end{array}
\]

The high energy vibration band can be attributed to a ring vibration and the lower to the exocyclic double bond vibration. These two bands most likely originate from strong coupling of the endo- and semicyclic C=C bonds, and not from the isolated vibrational modes. A detailed IR analysis has yet to be performed; only then may conclusions as to the extent of polarity in methylene cyclopropanes be reached.\(^7,16\)
Most of the methylenecyclopropenes hitherto known exhibit very complex ultraviolet spectra because the conjugated chromophores of the unsaturated substituents at the \( C_4 \)-carbon obscure information in the cross-conjugated species.\(^{1d,7}\) The UV absorptions of some dialkylsubstituted methylenecyclopropenes are listed below:

- **cyclohexane**
  - \( \text{nm}(4.30) \)
  - \( \text{nm}(4.27) \)
  - \( \text{nm}(4.24) \)

- **dichloromethane**
  - \( \text{nm}(4.09) \)
  - \( \text{nm}(4.43) \)
  - \( \text{nm}(4.44) \)

- **methanol**
  - \( \text{nm}(4.12) \)
  - \( \text{nm}(4.04, 4.20) \)
  - \( \text{nm}(4.24, 2.36) \)
Using the bathochromic effect of geminal dicyano substitution as obtained for ethylene compounds, and the positions of maxima in 38 and 41, the absorption of the parent methylene-cyclopropene, 1, is estimated to appear in the region of 205-215 nm. This absorption is in full agreement with MO predictions\textsuperscript{12} that the $\pi \rightarrow \pi^*$ transition for 1 will come near 200 nm.

As for the NMR spectroscopy of methylene-cyclopropenes, the increased charged density at the terminal methylene is reflected in an upfield shift of 0.9 ppm of the vinyl proton of 44 when compared with the model compound 45.\textsuperscript{25}

$^1H$-NMR data for alkyl- or H-substituted methylene-cyclopropenes are listed below:

\[ R = C_6H_5 \quad 8.85 \text{ ppm}^7 \]
\[ \alpha\text{-C-H Shifts} \]

\[
\begin{array}{ll}
R=\text{CH}_3 & 2.25 \text{ }^7_0 \\
R=\text{n-C}_3\text{H}_7 & 2.57 \text{ }^7_1 \\
R=\text{n-C}_4\text{H}_9 & 7.60 \text{ }^7_1 \\
R=\text{CH}_3, R'=\text{CN} & 7.44 \text{ }^7 (\text{CH}_3) \\
R=\text{n-C}_3\text{H}_7, R'=\text{CN} & 7.13 \text{ }^7 (\text{CH}_2(\alpha))^{34} \\
R=\text{CH}_3, R'=\text{COCH}_3 & 7.26 \text{ }^7 (\text{CH}_3) \\
\end{array}
\]

The chemical shift of methyl groups coupled with the internal chemical shift (\[ \alpha\text{-CH}_2 \text{ vs. } \beta\text{-CH}_2 \text{-protons} \]) of n-propyl groups has been utilized as a measure of determining the electron density of positively charged centers. Therefore, when the chemical shifts of the methyl groups as well as those of the \[ \alpha \text{- and } \beta\text{-methylene hydrogens of the propyl group of } 41 \sim \] were compared with those of \[ 46 \sim \], a 15% unit (+) charge on each propyl-substituted carbon was apparent which corresponded to approximately a 50% contribution of the dipolar resonance structure. 26,69
Although small, the consequence of the apparent single bond character of the methylenecyclopropene $C^3/C^4$ bond and the stabilization of the transition state of the rotation demonstrated$^{72}$ should be sufficient to lower the energy of rotation around this bond in comparison to simple ethylenic compounds.$^{73}$ The $^1H$-NMR spectra of the following asymmetrically substituted methylenecyclopropenes 47 - 50 proved to be temperature-dependent and showed reversible coalescence at specific temperatures characteristic of internal rotation processes:

\[
\begin{array}{ccc}
\text{CH}_3 & & \text{Ar} \\
\text{R}'' & & \text{Ar} \\
& \text{COR}' & \\
\text{Ar} & & \text{PhCO} \\
& \text{COCH}_3 & \\
\text{R} & & \text{CH}_3\text{CO} \\
& \text{COCH}_3 & \\
\end{array}
\]

47

\[
\begin{array}{ccc}
\text{Ph} & & \text{R} \\
\text{R}'' & & \text{COR}' \\
& \text{Ph} & \\
\end{array}
\]

48

\[
\begin{array}{ccc}
\text{Ph} & & \text{R} \\
\text{R}'\text{CO} & & \text{R}'' \\
\end{array}
\]

50

\[
\begin{array}{ccc}
\text{Ar} = \text{p-tolyl, p-anisyl, } \text{p-(tert-butyl)phenyl} \\
\text{R} = \text{CH}_3, \text{C(CH}_3)_2, \text{C}^\alpha \text{-naphthyl} \\
\text{R}' = \text{alkyl, aryl, NH-Ph, O-alkyl} \\
\text{R}'' = \text{CN, NO}_2, \text{acyl, aroyl}
\end{array}
\]
Methylenecyclopropenes of the type 50 which can exist either as the cis- or the trans-rotational isomer, most often are found as equilibrium mixtures of structures $\tilde{50}_A$ and $\tilde{50}_B$. Although separation into the stereoisomer was unsuccessful, the configurational and conformational assignments were achieved unambiguously. On the other hand, methylenecyclopropenes, $\tilde{51}$ and $\tilde{52}$, were crystallized as one specific configurational isomer which equilibrated in solution with its rotamer.

\[ \text{Ph} \quad \text{Ph} \]
\[ \text{CH}_3\text{CO}_2 \quad \text{CN} \quad \text{CN} \quad \text{CO}_2\text{CH}_3 \]
\[ \text{Ph} \quad \text{Ph} \]
\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{PhCO} \quad \text{CO}_2\text{Et} \quad \text{CO}_2\text{Et} \quad \text{COPh} \]

Gleicher, et al., interpreted the lowering of the rotational barrier in methylenecyclopropenes either by substituent stabilization of ground-state polarity leading to a decrease of $C^3/C^4$ double bond character or by stabilization of a more polar transition state due to substituents.
Reactions of Methylene cyclopropenes:

The majority of methylene cyclopropenes do not undergo defined thermal transformations which could very possibly be attributed to the differences in polarity due to the diversified substituents, especially those at the exocyclic position. Cycloreversion to yield alkynes and vinylidene carbene does not take place. Dimerization to give products of type $\sim$ is also not observed.

\begin{align*}
\begin{array}{c}
\includegraphics[width=0.8\textwidth]{reaction_diagram.png}
\end{array}
\end{align*}

\begin{equation}
(21)
\end{equation}

The photochemical reactions of methylene cyclopropenes are currently being investigated. Dimerization is reported as the major reaction in the photochemistry of 4,4-diacyl- and 4,4-dicyano methylene cyclopropene. Rare cases of hydrogen abstraction or solvent incorporation are also encountered.

The oxidation of methylene cyclopropenes is also dependent upon the specific methylene cyclopropene studied. 1,2-Diphenyl-4,4-dicyano and 4,4-diacetyl methylene cyclopropenes are very stable against alkaline $\text{H}_2\text{O}_2$. On the other hand, 1,2,3,4-tetraphenyl-5,6-dimethyl calicene, $\sim$, undergoes facile oxidation by atmospheric oxidation yielding the allenic
ketone, $\sim 56$, via an intermediate such as $\sim 55$ (Equation 22).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{Ph} & \quad \text{Ph} \\
\text{O}_2 & \quad \text{Ph} & \quad \text{Ph} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

(22)

Analogously, the oxidation of the cyclopropenylidene anthrone with ferric chloride in hydroxylic solvents gives the allene ketone after hydrolysis (Equation 23).

\[
\begin{align*}
\text{FeCl}_3 & \quad \text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} & \quad \text{-}2\text{e}^\theta \\
\text{CH}_3\text{OH} & \quad \text{-}2\text{H}^\theta \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

(23)

Reactions of methylenecyclopropenes towards electrophiles and nucleophiles are determined by their electron distribution. Protonation of the strongly colored methylenecyclopropenes, $\sim 57$ and $\sim 59$, lead to colorless cyclopropenium cations, $\sim 58$ and $\sim 60$, by the electrophilic attack at the exocyclic carbon.
The preferential attack of nucleophiles, such as water, alcohols, ammonia and other C-nucleophiles, is at the three-membered ring.\(^7\) 1,2-Diphenyl-4,4-diacetyl methylenecyclopropene, \(~12~\), undergoes attack by water, yielding the ring-opened triketone, \(~61~\). In the product, the separation of the phenyl-substituted carbons convincingly indicates attack of the nucleophile at \(C^1(2)\) of the methylenecyclopropene system.
Very recently in our laboratory 1,3-di-t-butyl-2-bromo-methylenecyclopropane was reacted with H₂O and the following products obtained.

A mechanism, explaining the formation of these products, is given in Scheme I (below).

Scheme I.
The 1,4-addition of H₂O to 15 or 16 would result in the formation of the intermediate 64, which could give 63 directly. 62 is expected to result from 1,2-addition of H₂O across the C³-C⁴ to yield 65, followed by collapse, as shown in Scheme I. This mechanism was further proven by D₂O reaction of 15 and 16 which resulted in one deuterium incorporation, as was predicted.

The nature of the final product formed in nucleophilic additions depends primarily on the nucleophile and the methylenecyclopropene. For example, 1,2-diphenyl-4,4-diacetyl-methylenecyclopropene, 12, reacts with ammonia and methyl amine.
to give the α-diacetylmethyleneazetidine, 66, while with other primary amines, the Schiff base, 67, and, with secondary amines, the cyclic aminal, 68, are obtained (see Scheme II).  

Nucleophilic attack at C of methylenecyclopropenes was also shown by Billups, et al., in the transformation discussed earlier (Equation 20).  

Methylenecyclopropenes react with systems containing multiple bonds in a variety of modes. Systems containing electron-deficient multiple bonds such as TCNE, MAA and ADD react with the exocyclic double bond of methylenecyclopropene. Typically, TCNE reacts with 1,2-diphenyl-4-carbothoxy methylenecyclopropene, 18, to give 69, the product of (2+2) cycloaddition (Equation 27).
With the calicene 70, TCNE attaches itself to five- and three-membered rings in a more complex cycloaddition mode yielding 71 (Equation 28).

\[
\begin{align*}
\text{70} & \quad \text{[4+2]} \quad \text{71} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{NC} & \quad \text{NC} \\
\text{CN} & \quad \text{CN} \\
\end{align*}
\]

(28)

Acetylene dicarboxylate and maleic anhydride did not react with methylenecyclopropanes; however, Prinzbach reported ready cycloaddition with calicene compounds.

There are various reports in the literature wherein the ring double bond in methylenecyclopropanes and calicenes behave as a dienophile towards some dienes in undergoing cycloaddition reactions. Therefore, reaction of 71 with diethylamino butadiene yields the Diels–Alder adduct 72 which subsequently undergoes elimination of the amine and ring opening to the dibenzo heptafulvene 73 (Equation 29).
Heptafulvenes can also be synthesized by a (2+2)cycloaddition of methylenecyclopropenes with the cyclobutadine, followed by ring opening as given in Equation 30.
The reactions of methylenecyclopropenes with electron-rich multiple bonds are reported to proceed via dipolar intermediates, 75 or 76, whose subsequent transformation is solely determined by the substituents at C4. 7

An illustrative example is the reaction of 4,4-dicyano-substituted methylenecyclopropenes with enamines to give the cross-conjugated dicyanomethylene compounds of the type 77. (Equation 31). 78

\[ \text{R} = \text{CH}_3, \text{Ph} \]
With enamines 4,4-diacyl methylenecyclopropanes produce compounds of the types 78 and 79, both of which undergo synthetically useful transformations. 78

\[
\text{Ph} \quad \text{Ph} \\
\text{RCO} \quad \text{COR}' \\
\text{Ph} \quad \text{Ph} \\
\text{N} \\
\text{R}'' \\
\text{Ph} \\
\text{Ph} \\
\text{RCO} \quad \text{COR}' \\
\text{O} \\
\text{R} \\
\text{R} \\
\text{Ph} \\
\text{Ph} \\
\text{N} \\
\text{R}'' \\
\text{Ph} \quad \text{Ph} \\
\text{RCO} \quad \text{COR}' \\
\text{O} \\
\text{R} \\
\text{R} \\
\text{Ph} \\
\text{Ph} \\
\text{N} \\
\text{R}''
\]

(32)

78

79

Schiff bases of the type 80 react with methylenecyclopropanes via their tautomeric vinylamine form to afford products, corresponding to "C-C" insertion. If the substituent on the C^4 is COOR, then the system 81 cyclizes by loss of alcohol, producing the 2-pyridones 82 (Equation 33). 7

\[
\text{Ar}-\text{C} = \text{N} - \text{R} \\
\text{R}''' - \text{CH} - \text{R}'''
\]

\[
\text{Ar} - \text{C} - \text{NHR} \\
\text{R}''' - \text{C} - \text{R}'''
\]

80

81

82

(33)
Diazoalkanes add across the C\textsuperscript{1}–C\textsuperscript{2} double bond of methylenecyclopropanes, as illustrated in the case of 1,2-di-phenyl-4,4-diacetyl methylenecyclopropene (Equation 34); the intermediate readily undergoes rearrangement to give 83.\textsuperscript{79} The mode of rearrangement of the intermediate leading to 83

\[ \text{Equation 34} \]

is dependent on the substituents of the starting methylenecyclopropane.\textsuperscript{79,80}

Calicenes, however, undergo attack by diazomethane across the exocyclic bond, followed by another addition of CH\textsubscript{2}N\textsubscript{2} to the ring double-bond.\textsuperscript{76}

\[ \text{Equation 35} \]
RESULTS AND DISCUSSION

The study reported here has as its goal the development, based on previously unreported precursors, of new routes to simple methylenecyclopropenes, including the parent hydrocarbon. The chemistry centers around the now familiar base-induced elimination-isomerization reaction of halocyclopropanes.¹⁹,²⁴

A number of approaches to methylenecyclopropene 1 seem reasonable.¹⁸,¹⁹ Compounds of the type 84 where X is some good leaving group would provide the most direct and unequivocal synthesis of 1. As of this writing, however, no syntheses of these compounds have been reported, although they have been inferred as intermediates in trapping experiments.²⁴

![Diagram of compounds 1, 84, 85, 86](image)

The 2-Halo-3-Methylmethyleneecyclopropanes, 85, are probably intermediates in dehydrohalogenation of gem-dihalocyclopropanes 86.¹⁹ In fact, use of 1,1-dichloro-2-methylcyclopropane, 87,¹⁹ as a precursor to 1 (discussed earlier on page 3) has been explored by Shields and Gardner.¹⁹ They concluded
that the elimination gave the intermediate 88 which then polymerized.

Base-catalyzed isomerization of the double bond around the ring and into the methyl group would not be expected since the intermediate cyclopropene anion is "anti-aromatic" and most likely too energetic to be generated under these conditions. However, reinvestigation of this reaction under the following conditions resulted in formation of a product.

Reaction of 87 with KOT-Bu in THF at -30° to -40° or DMSO at 15° for one hour gave the 2-t-butoxymethylenecyclopropane, 35, in 32% and 28% yields, respectively, after isolation by preparative glpc (Equation 36).

\[
\begin{align*}
87 & \xrightarrow{\text{KOT-Bu, THF or DMSO}} 35 \\
(36)
\end{align*}
\]

Compound 35 was characterized by comparison of its NMR and ir spectral data with the reported values. The formation of 35 is rationalized in terms of two possible paths. Path
a incorporates methylenecyclopropene as a reactive intermediate; whereas path b is merely a nucleophilic addition to the cyclopropene double bond followed by another dehydrochlorination and subsequent isomerization to (Scheme III).

Scheme III.

While the facile conversion of 89 to  cannot be occurring, nevertheless, path b which bypasses methylenecyclopropene cannot be eliminated on the basis of these results.

After moderate success here, we concentrated on the synthesis of 1, using compounds of the type 84 as precursors. 2,2-Dichloromethylenecyclopropane, 90, had been prepared by the addition of dichlorocarbene to allene, and seems to be a possible precursor to 89, and, in turn, to 1.
Although methods of reduction of gem-dihalocyclopropanes to monohalocyclopropanes,\textsuperscript{84,85} and gem-dihaloalkylidenecyclopropanes to monohaloalkylidenecyclopropanes\textsuperscript{86} are known, there are no reported applications of these methods to simple compounds of type 90.

Compound 90 was prepared initially by addition of dichlorocarbene (generated from ethyl trichloroacetate and NaOMe) using the method of Dolbier and Tarrant.\textsuperscript{83} 90 could not be purified from other reaction product of ethyl methyl carbonate by distillation since the two boil within a few degrees of each other. Therefore, a modified method whereby NaOn-Bu was used as a base was employed. The other product, then, is ethyl n-butyl carbonate which boils considerably higher than ethyl methyl carbonate, thus enabling separation of the dichlorocarbene adduct by distillation.

Addition of dichlorocarbene, generated by treatment of ethyl trichloroacetate with freshly prepared NaOn-Bu, to allene at -40°, followed by careful distillation, gave 90 in 19% yield. (Equation 37). Compound 90 exhibited NMR (CHCl\textsubscript{3}-d) absorptions at \(6.01\) (m, 1H, vinyl), 5.65 (m, 1H, vinyl), 2.15 (m, 2H, cyclopropyl). Attempted reduction of 90 with varying concentrations of lithium aluminum hydride or sodium borohydride in a number of solvents at several temperatures and reaction times all proved unsuccessful. When 90 was heated at 35° in the presence of tri-n-butyltin hydride (method of Kuivila\textsuperscript{86}) \textsuperscript{ca}. 90% of the starting material was recovered even after 16 hours.
Since this reaction proceeds by a free radical mechanism, we then explored methods of accelerating the initiation step by use of catalysts. Azobisisobutyronitrile (AIBN) was chosen for this purpose, since it is known to decompose under mild conditions - such as heating to 45° - to the cyanopropyl radical which initiates the free-radical chain. Irradiation was also chosen to further accelerate the initiating step.

Reaction of 90 with 1 equivalent of tri-n-butyltin hydride in the presence of a catalytic amount of AIBN at 55° and under irradiation from a Sunlamp for six hours resulted in a 50% yield of 2-chloromethylenecyclopropane (89). Compound 89

\[
\text{Cl} \quad \overset{(\text{n-butyl})_3\text{SnH}}{\text{AIBN}} \quad \overset{\text{h}}{\text{Cl}}
\]

(38)

was identified from its NMR and IR spectra. The NMR spectrum (CHCl₃-d) showed absorptions at \(2.05\) (m, 2H, cyclopropyl), \(3.65\) (m, 1H, cyclopropyl), \(5.60\) (m, 1H, vinyl) and \(6.01\) (m, 1H, vinyl). [For NMR and IR spectra of 89, see Appendix III, Figures 1a and 1b]. Compound 89 proved to be stable only at freezer temperature for 24 hours. When left at room temperature or stored for longer periods of time in the freezer (-5°), it decomposed to a black liquid which could not be identified.
Treatment of 91 with KOT-Bu in THF at -60° for one hour gave 35 in 62% yield after isolation by preparative glpc. [For NMR and IR spectra of 35, see Appendix III, Figures 2a and 2b]. One equivalent of 89 was then reacted with four equivalents of KOT-Bu and two equivalents of MeSH in DMSO to yield 2-thiomethylmethylene cyclopropane, 36, in 70% yield. [For NMR and IR spectra, see Appendix III, Figures 3a and 3b]. Since MeSH is a stronger acid than t-BuOH, the reaction medium contained two equivalents of KOT-Bu, two equivalents of t-BuOH and two equivalents of KSHMe when compound 89 was added.

Although the formation of 35 and 36 are rationalized readily in terms of methylenecyclopropene as a reactive intermediate which experiences addition of a nucleophile, another possible path is an S$_N$2' reaction on 89 to give 91 followed by
the series of events in Equation 40.

\[ \begin{array}{c}
\text{Ot-Bu} \\
\text{Cl}
\end{array} \xrightarrow{\text{89}} \begin{array}{c}
\text{Ot-Bu} \\
\text{Cl}
\end{array} \xrightarrow{\text{91}} \begin{array}{c}
\text{Ot-Bu} \\
\text{Cl}
\end{array} \xrightarrow{\text{92}} \begin{array}{c}
\text{Ot-Bu}
\end{array} \xrightarrow{\text{35}} (40) \]

Some precedent for the $S_{N2}'$ reaction is found in Equation 41, where 93 surprisingly undergoes what appears to be an $S_{N2}'$ reaction, giving 94.

\[ \begin{array}{c}
\text{Cl}
\end{array} \xrightarrow{\text{KOT-Bu}} \begin{array}{c}
\text{Cl}
\end{array} \xrightarrow{\text{KSM}} \begin{array}{c}
\text{MeS}
\end{array} \xrightarrow{\text{94}} (41) \]

An $S_{N2}$ displacement which would lead to 36 (or 35) directly from 89 was eliminated on the basis of the following blank reaction. Treatment of one equivalent of 89 with four equivalents of KSM, prepared from KOT-Bu and excess MeSH in DMSO, resulted in ca. 95% recovery of the starting material and no $S_{N2}$ reaction product 36. The mercaptide is, of course, not a sufficiently strong base to dehydrochlorinate 89.
Following the successful isolation and characterization of 89, attention was then focused on the synthesis of the precursor 95, which would lead to methylenecyclopropene 96.

\[
\begin{align*}
&\text{CH}_3 \quad \text{Cl} \\
&\quad \text{CH}_2 \\
&\quad \quad 95 \\
&\quad \text{CH}_3 \quad \text{Cl} \\
&\quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 \quad \text{CH}_2 \\
&\quad \quad 96
\end{align*}
\]

Compound 96 is of interest with regard to regiochemistry of nucleophilic addition to methylenecyclopropenes. Regiospecific addition at the more substituted position would, of course, also eliminate the \( S_N^2 \) process as a viable mechanism.

After Shields and Gardner\(^{19,24} \) who earlier postulated 95 as an intermediate in their studies on the dehydrohalogenation of 86, the reaction shown in Equation 42 was investigated.

\[
\begin{align*}
\text{CH}_3 \quad \text{Cl} & \quad \text{CH}_2 \\
\quad \quad 86 & \quad \text{KOT-Bu} \\
\text{CH}_3 & \quad \text{CH}_3 \quad \text{SCH}_3 \\
\quad \quad 97 & \quad \text{CH}_3 \text{SH}
\end{align*}
\]

Equation 42

97 was isolated as the major product in 35% yield, and exhibited NMR absorptions at \( \delta \) 1.10-1.38 (m, 2H, cyclopropyl), 1.40 (s, 3H, methyl), 2.10 (s, 3H, thiomethyl) and 5.35-5.55 (m, 2H, vinyl).
The formation of \(~\) can be rationalized either in terms of 2-methylmethylene cyclopropene, \(~\), as a reactive intermediate (path a of Scheme IV.) or by the sequence (path b) involving dehydrochlorination-addition-dehydrochlorination-double bond isomerization shown in Scheme IV. Since path b cannot be eliminated on the basis of the result obtained in Equation 42, a study to synthesize \(~\) and investigate its chemistry was undertaken.

Reaction of compound \(~\) with CH₃Li in ether at -40° gave 1,2-butadiene, \(~\), in 82% yield. It was necessary to collect
the diene in a cooled (-70°) trap. Since compound 98 could not be stored indefinitely, it was used immediately in the following reaction. Addition of dichlorocarbene \(^{90}\) (method of Skell) to 98 at -70° yielded 99 in 45° yield. The starting material 99 was prepared from 87 as shown in Equation 43.

Reduction of 99 with one equivalent of tri-n-butyltin hydride in the presence of a catalytic amount of AIBN at 70° and under irradiation from a Sunlamp for 12 hours afforded

\[
\begin{align*}
\text{CH}_2 & \quad \text{(n-butyl)\textsubscript{3}SnH} \\
\text{H}_3\text{C} & \quad \text{AIBN} \\
\text{Cl} & \quad \text{h\textgamma} \\
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{Cl} & \quad \text{H} \\
\text{99} & \quad \text{100}
\end{align*}
\]

2-chloro-3-methylmethylenecyclopropane, 100, in 45% yield as a mixture of geometrical isomers. Compound 100 was collected in a cold trap and stored in the freezer. It was characterized by its NMR and IR spectra. [For the NMR and IR spectra, see Appendix III, Figures 4a and 4b]. The NMR spectrum of 100 had absorptions at 5.65 (narrow multiplet, 1H, vinyl), 5.45 (narrow multiplet, 1H, vinyl), 3.72 (multiplet, 1H), 3.25 (multiplet, 1H), 1.55 (singlet, 3H, methyl), 1.45 (singlet, 3H, methyl) and 2.05 (multiplet, 1H).
Treatment of 100 with eight equivalents of KOT-Bu in THF at -30° to -40° for 30 minutes gave a black polymer which could not be identified. Since no starting material was recovered, the compound apparently eliminated to give the 2-methylmethylene cyclopropane which subsequently underwent double bond-isomerization to the exocyclic position giving dimethylenecyclopropane, 101. Compound 101 reported to undergo facile polymerization even at -10°. In accordance with the results obtained by Shields and Gardner, double bond isomerization is expected to be faster than nucleophilic addition when the nucleophile is $^{\theta}$O$t$-Bu.

To establish the fate of compound 96 in the presence of strong nucleophiles, the following two reactions were performed and the products isolated and identified.

Reaction of compound 100 with four equivalents of KOT-Bu and two equivalents of MeSH in DMSO for thirty minutes gave compound 97 as the major product in 43% yield after isolation by preparative glpc (Equation 45). Compound 97 exhibited
NMR absorptions at $\delta$ 1.00-1.38 (multiplet, 2H, cyclopropyl), 1.40 (singlet, 3H, methyl), 2.10 (singlet, 3H, thiomethyl) and 5.35-5.55 (multiplet, 2H, vinyl). [For NMR and IR spectra, see Appendix III, Figures 5a and 5b].

Treatment of one equivalent of compound 100 with 2.5 equivalents of KOT-Bu and ten equivalents of NaOMe in DMSO at 15° for one hour afforded 2-methoxy-2-methylmethylene cyclopropane, 102 (40%) and trans-2-methoxy-3-methylmethylene cyclopropane, 103 (21%). Shields and Gardner obtained compounds 102 and 103 in the same relative amounts when they carried out the dehydrochlorination of 1,1-dichloro-2,3-dimethylcyclopropane 86 with KOT-Bu-NaOMe. The ratio of 102 : 103 is about what one would expect from the addition of methoxide ion to 86.

\[
\begin{align*}
100 & \xrightarrow{\text{KOT-Bu NaOMe}} 102 \quad \text{CH}_2 \\
& \quad \text{CH}_3 \quad \text{OMe} \\
& \quad \text{CH}_3 \quad \text{OMe} \\
+ & \quad \text{CH}_2 \\
103 & \quad \text{OMe}
\end{align*}
\] (46)

The use of the small nucleophile methoxide ion eliminates the steric factor requirement dominating the transition state and favoring formation of 103. Instead, the relative stability of the carbanion intermediates becomes the more operative factor favoring formation of 102. It is not clear why Equation 45 should exhibit complete regiospecificity.
Although these results provide evidence against an 
$S_N2$ process, further direct evidence which completely eli-
minates this mechanism is found in a blank experiment showing 
that the reaction of compound 100 with $\text{MeS}^\ominus$, generated from 
$\text{KOT-Bu}$ and excess $\text{MeSH}$ in $\text{DMSO}$ results in ca. 95% recovery 
of the starting material and no other products.

As was mentioned earlier in the introduction, Billups and 
Blakeney$^{3,24}$ synthesized 1,2-dichloro-1-methylcyclopropane, 
$\sim 34$, as the starting material in their approach to the synthesis 
of methylenecyclopropene. Based on the preliminary microwave 
studies, compound $\sim 34$, which was isolated and purified in only 5% 
by preparative g LPC, was assigned the cis configuration.

In order to establish the configuration unequivocally and 
also find an alternate and more efficient method of purifica-
tion, the reaction leading to the formation of $\sim 34$ was reinves-
tigated. Addition of chloromethylcarbene, generated by the 

\[
\text{CH}_3 \quad \text{Cl} \\
\text{H} \quad \text{Cl} \\
\sim 34 \\
\text{CH}_3 \quad \text{Cl} \\
\text{H} \quad \text{Cl} \\
\sim 104
\]

method of Olah,$^{55}$ to vinyl chloride and a careful spinning band 
column distillation gave cis-1,2-dichloro-1-methylcyclopropane, 
$\sim 34$, and trans-1,2-dichloro-1-methylcyclopropane, $\sim 104$. The NMR
spectrum of 34 exhibited absorptions at $\sim 1.15-1.55$ (m, 2H, cyclopropyl), $1.65$ (s, 3H, methyl), $2.95-3.10$ (m, 1H) and $104$ at $0.89-1.09$ (m, 1H, cyclopropyl), $1.45-1.60$ (m, 1H, cyclopropyl), $1.72$ (s, 3H, methyl) and $3.31-3.51$ (m, 1H).

[For NMR and IR spectra of 34, see Appendix III, Figures 6a and 6b; for NMR and IR spectra of 104, see Appendix III, Figures 7a and 7b]. The cis and trans assignments were based on $^{13}$C-NMR and microwave studies, and the tentative assignment made by Billups was proven to be correct.

To explore the behavior of the trans isomer, identical trapping reactions were carried out, as hereinafter described. Reaction of 104 with KOT-Bu in THF at $-30^\circ$ to $-40^\circ$ for one hour gave the 2-t-butoxymethylene cyclopropane 35 in 32% yield,

\[
\begin{align*}
\text{KOT-Bu} & \quad \text{THF} \\
\text{CH}_2 & \\
\text{Ot-Bu} & \\
\text{CH}_3 & \\
\text{Cl} & \\
\text{Cl} & \\
\text{H} & \\
\text{104} & \\
\text{KOT-Bu} & \quad \text{CH}_3\text{SH} \\
\text{CH}_2 & \\
\text{SCH}_3 & \\
\text{36} & \\
\end{align*}
\]

(47)

after isolation by preparative glpc. One equivalent of 104 was reacted with six equivalents of MeSH in DMSO, producing the
2-thiomethylmethylene cyclopropane 36 in 50% yield after purification by preparative gcpe. As before, the formation of 35 and 36 is rationalized in terms of 1.

In our efforts to constantly upgrade the approaches presented thus far for the synthesis of methylene cyclopropene, an investigation of an efficient alternate synthesis of compounds of the type 105, where X is either chlorine or bromine, was undertaken.

\[
\begin{array}{c}
\text{CH}_3 \quad \text{X} \\
\text{CH}_3 \quad \text{X} \\
\text{X} \\
\text{X} \\
\end{array}
\]

105

\[
\begin{array}{c}
\text{CH}_3 \quad \text{X} \\
\text{H} \\
\end{array}
\]

106

Reduction of compounds of type 105 with tri-\(\eta\)-butyltin hydride, as previously described for 90, would then be expected to yield compounds bearing substituents as in 106, an alternate precursor to 1. Addition of dihalocarbenes to 2-halopropenes would be expected to give 105. Skell's method of adding dichlorocarbene to 2-chloropropene produced a very low yield of the expected adduct. However, addition of dibromocarbene, generated by treatment of bromoform with KO\(\eta\)-Bu, to 2-chloropropene at -70°, followed by a very careful distillation gave
1,1-dibromo-2-chloro-2-methylcyclopropane, 107, in 21% yield (Equation 48). [For the NMR and IR spectra of 107, see Appendix III, Figures 8a and 8b].

\[
\begin{array}{c}
\text{CH}_2\text{CCH}_3 \\
\text{Cl} \\
\end{array} \xrightarrow{\text{KOT-Bu, CHBr}_3, -70^\circ} 
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{Br} \\
\text{Br} \\
\end{array}
\]

107

In the presence of a catalytic amount of AIBN and under irradiation from a sunlamp, reaction of 107 with one equivalent of tri-n-butyltin hydride at 55° for three hours afforded cis- and trans-1-chloro-1-methyl-2-bromocyclopropane, 108 (70%).

\[
\begin{array}{c}
107 \\
\end{array} \xrightarrow{\text{(n-Butyl)}_3\text{SnH, AIBN, h}^\circ} 
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{Br} \\
\text{H} \\
\end{array}
\]

108

Compound 108 exhibited NMR absorptions at \(0.95-1.55\) (m, 4H), \(1.65\) (s, 3H), \(1.75\) (s, 3H), \(2.78-3.00\) (m, 1H) and \(3.25-3.55\) (m, 1H). [For the NMR and IR spectra of 108, see Appendix III, Figures 9a and 9b].
Reaction of 108 with KOT-Bu in THF at -30° to -40° for one hour gave 2-t-butoxymethylenecyclopropane, 35, in 30% yield, after isolation by preparative glpc (Equation 50).

The adduct 35 almost certainly arises from nucleophilic addition to methylenecyclopropane. The conversion of 108 → 35 could incorporate the following compounds 109 - 112 as potential intermediates.
Scheme VI shows how these four possible intermediates are incorporated. Intermediates 110 (path a) and 111 (path b) are expected to undergo double bond isomerization to 109.

Scheme VI.
As indicated earlier, the 1-alkylcyclopropenes undergo isomerization of the double bond faster than the addition of a good nucleophile.\textsuperscript{19} In strict analogy to 2-chloromethylene-cyclopropane (89) which, as discussed earlier, was isolated and convincingly shown to undergo dehydrochlorination to \textsuperscript{1},\textsuperscript{20} appearing in paths a, b and d - will similarly undergo dehydrobromination to give \textsuperscript{1}.

One equivalent of 108 was reacted with eight equivalents of KOt-Bu and two equivalents of MeSH in DMSO. Essentially this means that when 108 was added to the solution, there were six equivalents of KOt-Bu and two equivalents of KSMe. The product was 2-thiomethylmethylenecyclopropane 36 in 47\% yield.

At this point, a breakthrough in the field of methylene-cyclopropene chemistry was made, when it was discovered that \textsuperscript{1} can be generated in solution, transferred in the gas phase from flask to flask, and its chemistry investigated away from the medium in which it is generated. The choice of a non-nucleophilic base, namely KOH (alcoholic), for the generation of methylenecyclopropene, eliminates the possibility of a nucleophilic addition across the cyclopropene double bond. Instead, what is especially significant here is the observation that, upon treatment of either 2-chloromethylenecyclopropane (89) or \textit{cis}- and \textit{trans}-1-chloro-1-methyl-2-bromocyclopropane (108) with ethanolic KOH at 45°, a volatile compound is formed which could be trapped in a second reaction flask with \textsuperscript{2}Ot-Bu or \textsuperscript{2}SMe as the nucleophilic addition adduct.
Reaction of one equivalent of 89 with 1.5 equivalents of KOH in absolute ethanol at 45° generated a volatile compound which was passed into a slurry of KOT-Bu (three equivalents) in THF at 0° and gave 2-\text{-}t\text{-}butoxymethylene cyclopropane, 35 (Equation 51).

\[ 89 \xrightarrow{\text{KOH, EtOH, 45°}} \xrightarrow{\text{KOT-Bu, THF, 0°}} 35 \]

Treatment of 108 (one equivalent) with ethanolic KOH (three equivalents) at 55°, followed by passage of the volatile compound into a solution of KOT-Bu (three equivalents) in THF at 0°, afforded the same product.

When SMe (three equivalents) in DMSO was used as the nucleophile with one equivalent of either 89 or 108, the product in both cases was the 2-thiomethylmethylene cyclopropane 36 (Equation 52).
Lack of any kind of direct spectral evidence, coupled with our recent discovery of the generation of methylenecyclopropene \( \sim \) in solution, and transfer in the gas phase from flask to flask, prompted us to investigate its spectral properties. Due to its predicted instability, we then resorted to obtaining an NMR spectrum of \( \sim \) at low temperature (-50\(^\circ\)).

Methylenecyclopropene, generated by treatment of compound \( \sim \) with ethanolic KOH, was passed into a chilled (-60\(^\circ\)) CDCl\(_3\) and the NMR spectrum recorded. Weak absorptions at 5.65 (multiplet, 2H, exocyclic) and at 7.35 (multiplet, 2H, cyclopropene) were observed, but vanished after about four minutes. These signals are not inconsistent with methylenecyclopropene as a transient species which gains little stabilization from resonance with the aromatic dipole. A sizeable contribution from the dipole would lead to a shielding of the exocyclic
methylene which appears at § 5.65.

Attempts at obtaining either an infrared or microwave spectrum of \textsuperscript{\sim} \textsuperscript{1} have thus far proved unsuccessful. In the future, the low temperature-matrix technique, identical to that employed by Chapman and co-workers \textsuperscript{92} in their studies involving cyclobutadiene \textsuperscript{2}, may prove to be a viable route to obtaining the infrared spectrum of \textsuperscript{\sim} \textsuperscript{1}.

At this point, we focused our attention on investigating other chemical behavior of \textsuperscript{\sim} \textsuperscript{1} in addition to the nucleophilic additions.

All attempts to trap \textsuperscript{\sim} \textsuperscript{1} as a Diels-Alder adduct of 1,3-diphenylisobenzofuran in a "one-flask" reaction failed. Instead, only nucleophilic addition adducts were observed. A study was then undertaken to generate \textsuperscript{\sim} \textsuperscript{1} using Equation 51 (page 60), which would allow external trapping of methylenecyclopropene.

Treatment of either 2-chloromethylenecyclopropane, \textsuperscript{89}, or \textit{cis}- and \textit{trans}-1-chloro-1-methyl-2-bromocyclopropane, \textsuperscript{108}, with ethanolic KOH followed by passage of the gas into a chilled (-70°) solution of 1,3-butadiene in ether in a second flask gave 7-methylenebicyclo[4.1.0]hept-2-ene, \textsuperscript{114}, and not the expected Diels-Alder adduct of 7-methylenebicyclo[4.1.0]-hept-3-ene, \textsuperscript{113} (Equation 53).
Compound 114 exhibited NMR (CHCl₃-d) absorptions at δ 0.95-2.35 (6H) and 5.25-6.20 (4H). A prominent ir band at 11.20 μm is characteristic of methylenecyclopropanes. [For the NMR and IR spectra of 114, see Appendix III, Figures 10a and 10b].

An authentic sample of 114 was prepared using the method reported by Billups and co-workers93, wherein 8,8-dichloro-bicyclo[5.1.0]octane, 115, was treated with KOt-Bu in DMSO.
The NMR and IR absorptions and GLPC retention time of 114 obtained in Equation 53 was in full agreement with those obtained for the authentic sample in Equation 54.

A possible mechanism, leading to the formation of 114, is shown in Scheme VII.

\[
\begin{array}{ccc}
\text{H} & \text{B} \\
\text{H} & \text{B}
\end{array}
\]

\[
\begin{array}{ccc}
\text{H} & \text{B} \\
\text{H} & \text{B}
\end{array}
\]

Scheme VII.

The mechanism set forth in Scheme VII suggests that compound 113 does indeed form. However, the highly acidic allylic hydrogen may be abstracted by a trace of base. The resulting carbanion 116 can then undergo rapid protonation
by the solvent, yielding compound 114. The double bonds
being in conjugation could conceivably provide more stability
in 114 than in 113.

An attempt to synthesize 113 via Equation 55 also yielded
114, showing it to be the thermodynamically stable isomer.

\[
\begin{align*}
  &\text{CH}_3\text{CHCl}_2 \\
  &\text{n-ButLi} \\
  &\text{Et}_2\text{O} \\
  \rightarrow &\quad \text{Cl} \\
  &\text{CH}_3 \\
  \rightarrow &\quad \text{KOH} \\
  &\text{EtOH} \\
\end{align*}
\]

7-Chloro-7-Methylbicyclo[4.1.0]hept-3-ene, 117, was prepared
by a modification of the method employed by Binger.\textsuperscript{55} Chloro-
methylcarbene, generated by treatment of 1,1-dichloroethane
with n-ButLi in ether at \(-40^\circ C\) gave compound 117 in 86% yield.
Glpce analysis showed a mixture of the two isomers of 117 which
exhibited NMR (CHCl\textsubscript{3}-d) absorptions at $\delta 0.75-2.65$ (m, 12H),
1.35 (s, 3H, methyl), 1.55 (s, 3H, methyl), 5.45 (m, 2H, ole-
finic) and 5.65 (m, 2H, olefinic). [For the NMR and IR spectra
of 117, see Appendix III, Figures 11a and 11b].
The intermediacy of methylenecyclopropene is unequivocally established. Furthermore, methylenecyclopropene can be generated in solution, transferred in the gas phase from flask to flask and its chemistry investigated away from the medium in which it is generated. In the future, this method of generation, coupled with a low temperature-matrix technique may prove to be a viable route to obtaining the infrared spectrum of methylenecyclopropene, enabling its first direct spectral evidence.
EXPERIMENTAL SECTION

Nuclear Magnetic Resonance spectra were recorded on a Varian Model EM-390, XL-100 spectrometers in CDCl₃ solution and chemical shifts are expressed as parts per million downfield from internal tetramethylsilane. Infrared spectra were taken on neat compounds or in CHCl₃ solution, on a Beckmann IR-8 spectrometer. Ultraviolet spectra were recorded either in cyclohexane or ethanol solution using a Cary Model 17 spectrophotometer. Melting and boiling points are uncorrected. Glpc analyses were carried out on a Model 700 Hewlett Packard gas chromatograph using a thermal conductivity detector and helium as carrier gas. Specific columns and conditions are noted with the individual experiments. All reactions unless noted were run under an atmosphere of nitrogen.

Propene, methyl mercaptan, cis-2-butene and 1,3-butadiene were obtained from Matheson Company, Inc. Potassium t-butoxide and methyl lithium were supplied by Ventrom Corporation. Tri-n-butyltin chloride and cycloheptanone were obtained from the Aldrich Chemical Company. Hexadecyltrimethylammonium bromide (cetrimide) was obtained from Eastman Organic Chemicals. Allene and 2-chloropropene were obtained from Chemical Procurement Laboratories, Inc. Potassium hydroxide used in the elimination reactions was 86.6% and was from Fisher Scientific Company. Absolute ethanol was obtained from U. S. Industrial Chemicals Company. Chloroform used for dichlorocarbene additions was spectral grade and was obtained from Aldrich Chemical Company. 1,1-Dichloroethane and bromoform were reagent grade
and were distilled prior to use. Ether and tetrahydrofuran were distilled from sodium-benzophenone ketyl immediately before use.
Preparation of 1,1-Dichloro-2-Methylcyclopropane (87)

Propene (10 g, 0.2382 moles) was condensed in a trap and then allowed to boil rapidly into a chilled (-60°) slurry of KOt-Bu (26.68 g, 0.2382 moles) in 200 ml of pentane in a 500 ml three-necked flask. Chloroform (28.34 g, 0.2382 moles) was then added dropwise. A violent exothermic reaction took place and the mixture turned light brown in color. The mixture was kept at -60° for 45 minutes. On warming up the mixture to room temperature, excess propene was recovered unchanged. The reaction mixture was poured onto ice and the layers separated. The water layer was extracted with pentane. The extracts were combined and washed with saturated NaCl solution and dried (Na₂SO₄). Distillation gave 14.30 g (48%) of 87, b.p. 93°-95°.

Reaction of 1,1-Dichloro-2-Methylcyclopropane (87) with KOt-Bu in THF:

1,1-Dichloro-2-Methylcyclopropane, 87, (0.500 g, 4 mmole) was added dropwise to a mechanically stirred slurry of KOt-Bu (3.58 g, 32 mmole) in 20 ml of dry THF maintained at -30° to -40°. After stirring for one hour at this temperature, chilled water was added and the mixture extracted thrice with petroleum ether (20°-40°). The extracts were combined and washed eight times with water, then with saturated brine, and dried (Na₂SO₄). The solution was concentrated to ~2 ml by distillation.
GlpC analysis (10% Carbowax 20M on Anakrom ABS column at 65°) revealed one major and two higher boiling minor components. The major component had the same retention time as that of the authentic 2-\(t\)-butoxymethylenecyclopropane \(\sim\) as was determined by co-injection. Preparative glpc using the same column yielded 0.162 g (32%) of pure 2-\(t\)-butoxymethylenecyclopropane \(\sim\).

Preparation of 2,2-Dichloromethylenecyclopropane (90) \(\sim\)

Allene (80 g, 2 moles) was condensed in a one-liter three-necked flask, equipped with a mechanical stirring, dry-ice condenser and addition funnel with \(N_2\) inlet, containing 400 ml of pentane and freshly prepared NaOr-Bu (40 g, 0.4167 moles) which was cooled to -40°. Then, ethyl trichloroacetate (96 g, 0.5026 moles) was added all at once, and the mixture was allowed to warm slowly while stirring. At -10°, refluxing began, and at -8°, the solution turned a tar color. The mixture was allowed to warm overnight, and then 200 ml of \(H_2O\) was added. The aqueous layer was washed with 200 ml of pentane, the layers were combined and dried (\(Na_2SO_4\)), and distilled at atmospheric pressure through a one-foot vigreaux column to afford 12.36 g (19%) of 2,2-dichloromethylenecyclopropane \(\sim\), b.p. 95°-105°.

Preparation of Tri-\(n\)-butyltin hydride.

\(n\)-butyltin hydride was prepared by the Kuivila method.
To anhydrous ether (150 ml) in a 500 ml three-necked round-bottomed flask, which was cooled in an ice-water bath and fitted with a nitrogen purge system, an addition funnel and mechanical stirrer, was added LiAlH$_4$ (1.56 g, 0.0411 moles) and tri-n-butyltin chloride (32.5 g, 0.1000 moles). The mixture was stirred at bath temperature for 15 minutes, and then at room temperature for 3 hours. 1.6 ml of H$_2$O, 1.6 ml of 15% NaOH solution, and 5 ml of H$_2$O were consecutively added dropwise to the solution (caution: frothing). The reaction was then stirred until white solid precipitated. The reaction mixture was then filtered, poured into H$_2$O and extracted with ether. The aqueous layer was back-extracted with ether, the ether layers combined, washed with cold H$_2$O and with saturated NaCl solution, and then dried (Na$_2$SO$_4$). Solvent removal by rotary evaporation and subsequent distillation gave 23.4 g (81%) of tri-n-butyltin hydride, b.p. 50°-53°/0.20 mm.

Preparation of 2-Chloromethylenecyclopropane (89).

A 50 ml three-necked flask, equipped with a magnetic stirrer, reflux condenser with nitrogen inlet, and an addition funnel with a rubber serum septum, was flame-dried and cooled. 2,2-Dichloromethylenecyclopropane (4.10 g, 0.0333 moles) and a catalytic amount of AIBN (azobisisobutyronitrile) were placed in the flask. Tri-n-butyltin hydride (9.69 g, 0.0333 moles) was
then transferred to the addition funnel by a hypodermic syringe and then added dropwise while maintaining the temperature at 0°. After the addition was completed, the mixture was then heated to 55° and irradiation begun. The rxn was monitored by glpc (10% Carbowax 20 M on Anakrom ABS column operated at 65°C) every two hours; the starting material had disappeared completely at the end of six hours.

Purification was achieved by pumping off the product into a cold trap. 1.48 g (.0168 moles) (50%) of 2-chloro-methylene-cyclopropane, 89, was collected as a clear and colorless liquid.

NMR (CHCl₃-d) \[ \delta 2.05\text{m, } 2\text{H, cyclopropyl}, 3.65\text{m, } 1\text{H, cyclopropyl}, 5.60\text{m, } 1\text{H, vinyl}, 6.01\text{m, } 1\text{H, vinyl}. \]

For NMR and IR spectra of compound 89, see Appendix III, Figures 1a and 1b.

Reaction of 89 with KOT-Bu in THF:

In a 100 ml three-necked flask, fitted with a mechanical stirrer, addition funnel and nitrogen inlet, was prepared a slurry of KOT-Bu (2.55 g, 0.0227 moles) in 30 ml of dry THF. Maintaining the mixture at -60°, 2-chloromethylene-cyclopropane, 89, (0.500 g, 0.0057 moles) was added dropwise and the mixture stirred for one hour at this temperature. After allowing it to warm up to room temperature, H₂O was added and the mixture was extracted thrice with petroleum ether (20°-40°). The extracts were combined and washed 8-10 times with H₂O. Drying (Na₂SO₄) and concentration of the solution to ~3 ml by distillation at atmospheric pressure gave a greenish liquid. Glpc analysis
(10% Carbowax 20 M on Anakrom ABS operated at 65°) showed no starting material. The major product had the same retention time as that of an authentic sample as was checked by coinjection. Preparative glpc on the same column yielded 0.4439 g (62%) of 2-\textsuperscript{t}-butoxymethylenecyclopropane (35).

For NMR and IR spectra of 35, see Appendix III, Figures 2a and 2b.

Reaction of 89 with KO\textsubscript{t}-Bu – MeSH in DMSO:

Pre-condensed MeSH (1.09 g, 0.0227 moles) was distilled into a slurry of KO\textsubscript{t}-Bu (5.09 g, 0.0454 moles) in 20 ml of dry DMSO. After stirring at 15° for 15 minutes, compound 89 (1 g, 0.0114 moles) was added dropwise followed by an additional 30-minute stirring. The mixture was poured onto ice and extracted thrice with petroleum ether (20°–40°). The extracts were combined, washed with H\textsubscript{2}O, and then with saturated NaCl solution. After drying (Na\textsubscript{2}SO\textsubscript{4}), the solution was concentrated to 3 ml by distillation at atmospheric pressure. Glpc analysis (10% Carbowax 20 M on Anakrom ABS and 20% SE-30 on Chromosorb P) showed only one product with a distinctly different retention time than that of the solvent. Preparative glpc (20% SE-30 on Chromosorb P column at 85°) gave 1.14 g (70%) of 2-thiomethylmethylenecyclopropane, 36. Glpc retention time, NMR and ir spectral properties compared in full agreement with the known sample.

For NMR and IR spectra of 36, see Appendix III, Figures 3a and 3b.
Reaction of 89 with MeS\(^{2-}\) in DMSO:

In a 50 ml three-necked flask a solution of KOT-Bu (1.14 g, 0.0102 moles) was prepared in 20 ml of dry DMSO. Precondensed MeSH (2.46 g, 0.0515 moles) was then allowed to boil into this mixture while maintaining the temperature at 15°. After stirring for 15 minutes, compound 89 (0.300 g, 0.0034 moles) was added dropwise and the mixture was stirred an additional 30 minutes. The mixture was poured onto ice slush and extracted with petroleum ether thrice and the extracts were then combined and washed thrice with \(\text{H}_2\text{O}\) and then thrice with a saturated NaCl solution. Drying (Na\(_2\)SO\(_4\)) and concentration of the solution to ~3 ml by atmospheric distillation afforded a light yellow liquid. GLPC analysis (10% Carbowax 20 M on Anakrom ABS column operated at 65°) showed >95% recovery of starting material and no presence of the sulfide 36.

Preparation of cis-1,1-Dichloro-2,3-dimethylcyclopropane (86).

Cis-2-butene (5 g, 0.0893 moles) was condensed in a trap and then poured rapidly into a cooled (-50°) slurry of KOT-Bu (10 g, 0.0893 moles) in 150 ml of pentane in a 250 ml three-necked flask. Chloroform (10.63 g, 0.0893 moles) was then added dropwise. The temperature of the solution was allowed to rise to 10° near the end of the addition. After stirring
for thirty additional minutes, the reaction mixture was poured onto ice and the layers separated. The aqueous layer was extracted with pentane. The extracts were combined and washed with saturated NaCl solution and dried over Na₂SO₄. Distillation afforded 6.21 g (50%) of 86, b.p. 120°-124°.

Reaction of 1,1-Dichloro-2,3-Dimethylcyclopropane (86) with KOT-Bu - MeSH in DMSO.

Compound 86 (2 g, 0.0148 moles) was added to KOT-Bu (16.2 g, 0.1480 moles) and MeSH (2.78 g, 0.0592 moles) in 100 ml of DMSO in a 250 ml flask. The product was worked in the same manner as described previously for 36. Distillation gave 0.5812 g (35%) of a product, b.p. 115°-120°, which was identified to be compound 97 by coinjection with a known sample and comparison of the NMR and ir data with the reported values. An analytical sample was obtained by preparative glpc (10% Carbowax 20 M on Anakrom ABS column at 80°).

Preparation of 1,2-butadiene (98)

A 500 ml three-necked flask, equipped with a magnetic stirrer, addition funnel and a dry ice condenser with nitrogen inlet, was charged with compound 87 (11 g, 0.0879 moles) and 200 ml of anhydrous ether. Maintaining the mixture at -30° to -40°, 1.6 M CH₃Li (3.12 g, 0.1407 moles) was added dropwise and the product was collected in a cooled (-70°) trap. After
stirring for another thirty minutes, excess CH₃Li was destroyed by careful and dropwise addition of H₂O.

3.9 g (82%) of 1,2-butadiene (98) was collected and immediately used in the next step, which consisted of the addition of dichlorocarbene.

Preparation of 2,2-Dichloro-3-Methymethylene cyclopropane (99).

A 100 ml three-necked flask, equipped with a dry ice condenser, mechanical stirrer and a dip tube, was charged with KO-t-Bu (2.85 g, 0.0255 moles) and 40 ml of pentane. Maintaining the mixture at -70°, freshly made, condensed 1,2-butadiene 98 (3.9 g, 0.0732 moles) was allowed to boil into the solution. At this temperature, chloroform (3 g, 0.0255 moles) was added. A violent exothermic reaction took place and the mixture turned tan in color. One hour of additional stirring at -70° was then followed by allowing the mixture to warm up to room temperature. H₂O was added and the product extracted into pentane. The layers were separated, and the water layer back-extracted twice with pentane. The extracts were combined, washed with saturated NaCl solution, and dried (Na₂SO₄). Solvent removal afforded 2.43 g (70%) of crude 99. Glpc analysis (10% Carbowax on Anakrom ABS column at 100°) showed one major product and two minor products. Further purification was achieved by a very careful distillation through a one-foot vigreux column, which gave 1.56 g (45%) of 2,2-dichloro-3-methymethylene cyclopropane (99), b.p. 135°-138°.
Preparation of 2-Chloro-3-Methylmethylenecyclopropane (100)

Tri-n-butyltin hydride (6.42 g, 0.0221 moles) was added dropwise to compound 99 (3 g, 0.0221 moles) and catalytic amount of AIBN in a 50 ml flask. The mixture was heated to 70° and irradiation started. The rxn was monitored by glpc analysis (10% Carbowax 20 M on Anakrom ABS column at 95°) every 30 minutes; the starting material disappeared completely at the end of 12 hours. The product was purified by pumping it off into a cold trap; ca. 1 g (45%) of 2-chloro-3-methylmethylenecyclopropane (100) was collected.

NMR (CHCl₃-d) § 5.65 (narrow multiplet, 1H, vinyl), 5.45 (narrow multiplet, 1H, vinyl), 3.72 (multiplet, 1H), 3.25 (multiplet, 1H), 1.55 (singlet, 3H, methyl), 1.45 (singlet, 3H, methyl) and 2.05 (multiplet, 1H).

For NMR and IR spectra of 100, see Appendix III, Figures 4a and 4b.

Reaction of 100 with KOT-Bu in THF:

In a dry 100 ml three-necked flask was prepared a solution of KOT-Bu (2.64 g, 0.0235 moles) in 20 ml of dry THF. To the chilled (-30° to -40°) slurry was added dropwise compound 100 (0.300 g, 2.94 moles). The mixture instantly turned black and it was stirred for an additional thirty minutes. A black polymer-like substance was formed. Attempts to dissolve it in various organic solvents were unsuccessful. The mixture was
extracted with petroleum ether, the extracts combined and then washed with saturated brine. Drying (Na₂SO₄) and solvent removal was followed by glpc analysis (10% Carbowax 20 M on Anakrom ABS at 80°) which did not reveal the presence of either the starting material or any other product.

Reaction of 100 with KOt-Bu - MeSH in DMSO.

In a 100 ml three-necked flask was prepared a slurry of KOt-Bu (4.34 g, 0.0389 moles) and 50 ml dry DMSO. Maintaining the mixture at 15°, pre-condensed MeSH (1 g, 0.0208 moles) was distilled into the flask and the mixture stirred for 15 minutes. 100 (1 g, 9.71 mmole) was then added dropwise and the mixture stirred an additional 30 minutes. The product was worked up as described before for 36. Distillation gave 0.498 g (45%) of the product, b.p. 120°-123°. Glpc analysis (10% Carbowax 20 M on Anakrom ABS column at 80°) showed one minor (4.6%) and one major component (92%). Preparative glpc afforded 0.451 g (43%) of the major component which was identified to be 97 by comparison with an authentic sample. Preparative glpc of the minor component was unsuccessful.

For NMR and IR spectra of 97, see Appendix III, Figures 5a and 5b.

Reaction of 1-Chloro-2-Methylmethylenecyclopropane (100) with NaOMe* and KOtBu.

In a 100 ml three-necked flask, equipped with a mechanical stirrer nitrogen purge system and an additional funnel, was prepared a solution of NaOMe (5.82 g, 0.1078 moles) and KOtBu

*NaOMe was freshly prepared from Na and methanol; excess methanol was removed by distillation.
(2.72 g, 0.0243 moles) in 30 ml of dry DMSO. Compound 100 (1 g, 0.0097 moles) was added dropwise. The mixture was then stirred for one hour and monitored by withdrawal of 1-ml aliquots periodically at intervals of 15 minutes. Aliquots were shaken with 10 ml of water and 1 ml of pentane and frozen in dry ice-acetone slush to permit decantation of the pentane solution for glpc analysis (10% Carbowax 20 M on Anakrom ABS column at 60°). At the end of 1.25 hours, cold water was added and the mixture was extracted with pentane. The usual processing of the extract and removal of solvent yielded 0.746 g of flash-distilled product. Glpc showed two components with distinct retention times, component A (31%) and component B (64%). Separation by preparative glpc gave 0.205 g (21%) of trans-2-methoxy-3-methylmethylene cyclopropane (103) and 0.385 g (40%) of 2-methoxy-2-methylmethylene cyclopropane (102).

Reaction of 100 with MeS\(^\oplus\) in DMSO.

 Compound 100 (0.500 g, 4.91 mmol) was added to a slurry of KOtBu (1.65 g, 0.0147 moles), 15 ml of dry DMSO and MeSH (3.54 g, 0.0737 moles) using the same procedure as described previously for 89. The work-up followed the same procedure. Glpc analysis (10% Carbowax 20 M on Anakrom ABS column at 95°) revealed ca. 95% recovery of starting material and no other products.
Preparation of cis- and trans- 1,2-Dichloro-1-Methylcyclo-propane (34) and (104)

Compounds 34 and 104 were prepared by Mr. J. D. Buynak using the synthesis of Olah.

NMR (CHCl₃-d)  1.15-1.55 (m, 2H, cyclopropyl), 1.65 (s, 3H, methyl), 2.95-3.10 (m, 1H).

For NMR and IR spectra of 34, see Appendix III, Figures 6a and 6b.

NMR (CHCl₃-d)  0.89-1.09 (m, 1H, cyclopropyl), 1.45-1.60 (m, 1H, cyclopropyl), 1.72 (s, 3H, methyl) and 3.31-3.51 (m, 1H).

For NMR and IR spectra of 104, see Appendix III, Figures 7a and 7b.

Reaction of 104 with KOt-Bu in THF.

In a 50 ml three-necked flask, equipped with a mechanical stirrer, addition funnel and a nitrogen purge system, a slurry of KOt-Bu (3.23 g, 0.0288 moles) was added in 20 ml of THF. Maintaining the reaction temperature at -30° to -40°, compound 104 (0.450 g, 0.0036 moles) was added dropwise. After stirring for one hour at -30° to -40°, H₂O was added and the solution extracted three times with petroleum ether (20°-40°). The pet ether layers were combined and washed repeatedly with H₂O. After drying (Na₂SO₄), most of the petroleum ether was removed by rotary evaporation. GLpc analysis was performed on a 10% Carbowax 20 M on Anakrom ABS column operated at 65°; only a major and a few minor products were present. Preparative GLpc yielded 0.1451 g (32%) of 2-t-butoxymethylene cyclopropane (35).
Reaction of 104 with KOT-Bu - MeSH in DMSO.

MeSH (0.62 g, 0.0128 moles) was condensed in a cold trap and then distilled into a slurry of KOT-Bu (4.30 g, 0.0384 moles) in 50 ml of dry DMSO at 15° by means of a gas inlet tube inserted below the surface of the solution in a 100 ml three-necked flask. After stirring for 15 minutes, compound 104 (0.800 g, 0.0064 moles) was added dropwise. After stirring for an additional thirty minutes, the rxn mixture was poured onto ice and extracted three times with petroleum ether (20°-40°). The pet ether layers were combined, washed with H₂O and with saturated NaCl solution, and dried (Na₂SO₄). The solution was concentrated to ~2 ml by distillation at atmospheric pressure. Preparative glpc (10% Carbowax on Chromosorb W column at 65°) gave 0.32 g (50%) of the sulfide 36.

Preparation of 1,1-dibromo-2-chloro-2-methylcyclopropane (107)

In a 500 ml three-necked flask, equipped with a dry ice condenser, mechanical stirrer, addition funnel and nitrogen inlet, was prepared a slurry of KOT-Bu (44 g, 0.3929 moles) in 200 ml of petroleum ether (20°-40°). The slurry was then cooled to -70° and stirred at this temperature for 30 minutes. Maintaining the bath temperature at -70°, 2-chloropropene (20 g, 0.2632 moles) was added all at once and the mixture stirred for an additional thirty minutes. Bromoform (98 g, 0.3874 moles) was then added dropwise over a period of two hours. The mixture
turned dark tan, and then turned black before all of the bromoform was added. After the addition was completed, the mixture was allowed to stir at -70° for one hour, followed by a gradual warming to room temperature, and then stirring for an additional thirty minutes. H₂O was then added and the mixture extracted into petroleum ether (20°-40°). The black polymer-like substance was separated out by filtration. The organic layer was then separated out, and the aqueous layer back-extracted twice with pet ether. The extracts were combined and washed with both H₂O and with saturated NaCl solution. Drying (Na₂SO₄) and solvent removal in vacuo afforded 25.5 g (40%) of crude 107. Further purification was accomplished by distillation to yield 13.1 g (21%) of 107, b.p. 35°-38°/0.6 mm. Glpc analysis (20% SE-30 on Chromosorb P operated at 170°) showed ca. 98% purity of the distilled product.

For NMR and IR spectra of 107, see Appendix III, Figures 8a and 8b.

Preparation of 1-Bromo-2-Chloro-2-Methylcyclopropane (108)

A 50 ml three-necked flask, equipped with a magnetic stirrer, addition funnel with a serum septum, and reflux condenser with nitrogen inlet, was flame-dried and cooled. After being charged with 20 ml of benzene, the reaction vessel was degassed by bubbling nitrogen through the solution for three hours. Compound 107 (6.52 g, 0.0263 moles) and a catalytic amount of AIBN were then added under a heavy purge of nitrogen pressure. Tri-n-butyltin hydride (7.65 g, 0.0263 moles) was
then added dropwise while maintaining the mixture at 0° by an ice bath. The mixture was then heated to 55° and irradiation begun. The reaction was monitored by taking aliquots at thirty-minute intervals and analyzing them by thin-layer chromatography using CH₂Cl₂ as the eluent. Starting material disappeared at the end of three hours. The reaction mixture was distilled at atmospheric pressure using a micro distillation apparatus to afford 3.11 g (70%) of 1-bromo-2-chloro-2-methylcyclopropane 108, b.p. 100°-103°. Glpc analysis (20% SE-30 on Chromosorb P, operated at 155°) indicated a mixture of the two isomers of 108.

NMR (CHCl₃-d) δ 0.95-1.55(m, 4H, cyclopropyl), 1.65(s, 3H, methyl), 1.75(s, 3H, methyl), 2.78-3.00 (m, 1H), 3.25-3.55(m, 1H).

For NMR and IR spectra of 108, see Appendix III, Figures 9a and 9b.

Reaction of 2-bromo-1-chloro-1-methylcyclopropane (108) with KOt-Bu in THF:

A 50 ml three-necked flask, equipped with a mechanical stirrer, addition funnel, and nitrogen inlet, was charged with KOt-Bu (2.65 g, 0.0237 moles) and 20 ml of dry THF. Compound 108 (0.5 g, 0.0029 moles) was added dropwise while maintaining the reaction temperature at -30° to -40°. After stirring for an additional one hour at this temperature, H₂O was added and the product extracted three times into petroleum ether (20°-40°). The extracts were combined and washed repeatedly with equal volumes of H₂O and then with saturated NaCl solution.
After drying (Na₂SO₄), the solution was concentrated 3 ml by distillation at atmospheric pressure. Glpc analysis (10% Carbowax 20 M on Anakrom ABS column at 65°) indicated only one product with a retention time different from the solvent. Co-injection with an authentic sample confirmed the identity of the product. Preparative glpc on the same column gave 0.110 g (30%) of 2-tert-butoxymethylenecyclopropane (35). The NMR and ir spectral data were in agreement with the values reported earlier.

Reaction of 108 with KOT-Bu - MeSH in DMSO.

Compound 108 (1 g, 0.0058 moles) was added dropwise to KOT-Bu (5.20 g, 0.0464 moles) and MeSH (1.12 g, 0.0232 moles) in 50 ml of dry DMSO in a 100 ml flask. The product was worked up using the same procedure as described before for 36. Preparative glpc (10% Carbowax on Chromosorb W column at 65°) gave 0.27 g (47%) of the sulfide 36.
Reaction of 2-Chloromethylenecyclopropane (89) with Ethanolic KOH Followed By Trapping with \( ^\circ \text{Ot-Bu} \) in THF:

A 10 ml two-necked flask, equipped with a magnetic stirrer, a gas inlet system and a serum septum, and a 25 ml one-necked flask fitted with a dip tube, were assembled. Tygon tubing connected the gas inlet adapter to the dip tube. The first flask was charged with KOH (0.478 g, 8.54 mmoles) and 5 ml of absolute ethanol, while a slurry of KO\( ^\circ \)-Bu (1.91 g, 0.0171 moles) in 15 ml of dry THF was prepared in the second flask. The alcoholic KOH was heated in an oil bath to 45°. 2-Chloromethylenecyclopropane 89 (0.500 g, 5.68 mmoles) was then added dropwise by use of a syringe to the first flask, and the gas was passed through the dip tube into the slurry maintained at 0°. The mixture was stirred at 0° for three hours. Water was added and the mixture extracted with petroleum ether twice. The petroleum ether extracts were combined and washed repeatedly with water. After drying (\( \text{Na}_2\text{SO}_4 \)), most of the solvent was removed by rotary evaporation and then concentrated by distillation at atmospheric pressure to 2 ml of a yellow solution. GLPC analysis (10% Carbowax 20 M on Anakrom ABS column at 65°) revealed only one product with a distinctly different retention time than that of the solvent. Coinjection with a known sample showed the product to be 2-t-butoxymethylenecyclopropane (35). NMR spectrum further confirmed this result.
Reaction of 2-Bromo-1-Chloro-1-Methylcyclopropane (108) with Ethanol KOH Followed By Trapping With ô-OT-Bu in THF.

By adding 2-bromo-1-chloro-1-methylcyclopropane (108) (0.500 g, 2.96 mmole) to an ethanolic solution of KOH (0.500 g, 8.88 mmole) heated to 55°, Methyleneccyclop propane, generated as described above, was passed into a second flask containing a slurry of KOt-Bu (1.32 g, 0.0118 moles) in 10 ml of dry THF, maintained at 0°. The product was worked up in the same manner as described above. GLPC analysis (10% Carbowax 20 M on Analasrom ABS column at 65°) revealed only one product with an identical retention time as that of 35. NMR was in full agreement with that of an authentic sample.

Reaction of 89 with Ethanol KOH Followed By Trapping With ô-SMe in DMSO.

Using the same procedure as described above, methyleneccyclopropane was generated from 89 (0.500 g, 5.68 mmole) and was passed into a slurry of KOt-Bu (1.91 g, 0.0171 moles) and excess MeSH in DMSO at 15°. An identical work-up was followed by glpc analysis (10% Carbowax on Chromosorb W column at 65°) which showed a product with a retention time identical to that of a known sample of 2-thiomethylmethylenecyclopropane (36). NMR spectrum further confirmed this result.
Reaction of 108 with Ethanol KOH Followed By Trapping
With $^6$SMe in DMSO.

Methylenecyclopropene was generated from 108 and passed into a slurry of K$^6$SMe - prepared from KO$_2$-Bu and excess CH$_3$SH - in DMSO at 15°. After an identical work-up, glpc analysis (10% Carbowax on Chromosorb W column at 65°) showed a product with an identical retention time as that of an authentic sample of 36. NMR was also in full agreement with that of an authentic sample.

Reaction of 89 with Ethanol KOH Followed By A Diels-Alder Addition with 1,3-Butadiene.

In a 10 ml two-necked flask, was prepared a solution of KOH (0.956 g, 0.0171 moles) in 8 ml of absolute ethanol. The mixture was then heated in an oil bath to 45°. In a 25 ml three-necked flask, equipped with a dry ice condensor, magnetic stirrer and two dip tubes, was placed 10 ml of diethyl ether. Compound 89 (1 g, 0.0114 moles) was then syringed dropwise to the alcoholic KOH while 2 ml of pre-condensed 1,3-butadiene was allowed to boil into the second flask, maintained at -70°. Methylenecyclopropene generated in situ was passed into the second flask via a dip tube extending below the level of the ether solution. After stirring at -70° for fifteen minutes, the dry ice bath was replaced by an ice bath and the mixture stirred at 0° for two hours. Excess butadiene was allowed to
evaporate and the ether was then removed by distillation to afford 95 mg of a clear and foul-smelling liquid. GLPC analysis (20% SE-30 on Chromosorb P column at 135°) showed one major and two minor products. The major product was identified by coinjection with an authentic sample and comparisons of NMR and IR spectra to be 7-methylenebicyclo[4.1.0]-hept-2-ene, (114).

NMR (CHCl₃-d) δ 0.95-2.45 (m, 6H), 5.25 (m, 2H, olefinic),
5.35-6.25 (m, 2H, exocyclic).

A prominent IR band at 11.29 μ (methylene cyclopropane).

For NMR and IR spectra of 114, see Appendix III, Figures 10a and 10b.

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Reaction of 108 with Ethanoic KOH Followed By A Diels-Alder Addition with 1,3-Butadiene.

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In a 10 ml two-necked flask, was prepared a solution of KOH (0.9821 g, 0.0175 moles) in 8 ml of absolute ethanol. The mixture was then heated in an oil bath to 55°. In a 25 ml three-necked flask, equipped with a dry ice condenser, magnetic stirrer and two dip tubes, was placed 10 ml of diethyl ether. 2-Bromo-1-Chloro-1-Methylcyclopropane, 108 (1 g, 5.85 mmoles) was then syringed dropwise to the alcoholic KOH while 2 ml of 1,3-butadiene which had been pre-condensed in a trap was allowed to boil into the ethereal flask. Methylene cyclopropene, generated, was passed into the second flask through
one of the dip tubes extending below the level of the ether solution. The ethereal mixture was stirred at 0° for two hours. Excess butadiene was allowed to evaporate and the ether was then removed by distillation to afford 0.110 g of a clear and foul-smelling (almost identical to the smell of benzocycloprenene) liquid. Glpc analysis (20% SE-30 on Chromosorb P column at 135°) showed one major and traces of two minor products. Preparative glpc of the major product yielded 90 mg of pure 7-methylenebicyclo-[4.1.0]-hept-2-ene (114) as was established by coinjection with an authentic sample and comparisons of NMR and ir spectra.

Preparation of Cycloheptanol.

In a dry 250 ml three-necked flask, equipped with a reflux condenser with nitrogen inlet, a mechanical stirrer and an addition funnel, were placed LiAlH₄ (3.53 g, 0.0931 moles) and 125 ml of anhydrous ether. A solution of cycloheptanone (20 g, 0.1786 moles) in 30 ml of anhydrous ether was added, dropwise and with stirring, to the reaction flask at a rate which maintained gentle refluxing of the solvent. After the addition was complete, the reaction solution was refluxed for and additional thirty minutes and then allowed to cool; 3.5 mg of H₂O, 3.5 ml of 15% NaOH solution, and 11 ml of H₂O were consecutively added dropwise to the solution (caution: frothing).
The reaction was then stirred until the precipitation of white solids. The reaction mixture was then filtered, poured into 200 ml of cold aqueous 10% \( \text{H}_2\text{SO}_4 \). The ether layer was separated and the residual aqueous phase was extracted with three 100-ml portions of ether. The combined ether solutions were washed successively with \( \text{H}_2\text{O} \) and saturated aqueous \( \text{NaHCO}_3 \) solution, and then dried over \( \text{MgSO}_4 \). The ether was removed by distillation through a one-foot Vigreaux column, and the residue was distilled under reduced pressure to yield 14.25 g (70%) of pure cycloheptanol, b.p. 93°-95°/25 mm Hg.

Preparation of Cycloheptene.

In a 100 ml flask, fitted with a magnetic stirrer and distilling head, were placed cycloheptanol (12 g, 0.1053 moles) and 5 ml of concentrated sulfuric acid, and the flask was connected to a condenser and receiver surrounded by an ice bath. It was then placed in an oil bath which was heated to 170°-180°. The distillation was continued until only a small residue remained and the smell of sulfur dioxide was apparent. Toward the end of the distillation the temperature was raised to 190°. The receiver was kept cold during the entire distillation, which required two hours. The distillate was saturated with salt, and the cycloheptene was separated from the water layer. After drying with calcium chloride, it was fractionated through an efficient one-foot vigreaux column. The fraction boiling at 112°-115° was collected. The yield of cycloheptene was 8.6 g (85%).
Preparation of 8,8-dichlorobicyclo[5.1.0]octane (115).

Compound 115 was prepared using Skell's method. A 100 ml three-necked flask was equipped with a mechanical stirrer, a reflux condenser and an addition funnel. The system was flushed out with nitrogen and KOT-Bu (5.84 g, 0.0521 moles) and pentane (60 ml) were added. The stirred suspension was cooled to 0°-5° with an ice bath. Freshly prepared and distilled cycloheptene (5 g, 0.0521 moles) was introduced rapidly through the addition funnel, and chloroform (6.25 g, 0.0526 moles) was added dropwise over a course of thirty minutes. The resulting mixture was stirred for an additional thirty minutes and then 20 ml of H2O was added to dissolve all the precipitated salts. The layers were separated and the aqueous phase extracted with two 50-ml portions of n-pentane. The pentane extracts were combined, washed with saturated NaCl solution, and dried over Na2SO4. The solvent was then removed to give 4.2 g (45%) of 8,8-dichlorobicyclo-[5.1.0]octane (115) b.p. 61°-63°/.8 mm Hg.

Preparation of 7-Methylenebicyclo[4.1.0]hept-2-ene (114).

Compound 114 was prepared by Billups' method. In a 50 ml three-necked flask, equipped with a mechanical stirrer, nitrogen purge system and an additional funnel, was prepared a solution of KOT-Bu (5.27 g, 0.0470 moles) in 20 ml of dry
dimethyl sulfoxide; 8,8-Dichlorobicyclo[5.1.0]octane (115) (4.2 g, 0.0235 moles) was added dropwise with stirring over a period of ten minutes. After stirring for one hour, H₂O was added and the aqueous layer extracted with petroleum ether (20°-40°), then washed with saturated NaCl solution and dried over Na₂SO₄. The solvent was then removed by distillation affording 1.25 g (48%) of crude 114. Further purification was achieved by a very careful distillation to give 0.98 g (40%) of 114 (25°/0.25 mm). Compound 114 exhibited NMR and IR absorption in full agreement with the reported values.

NMR (CHCl₃-d) δ 0.95-2.45(m, 6H), 5.25(m, 2H, olefinic), 5.35-6.25(m, 2H, exocyclic).

Prominent IR band at 11.29 μ (methylenecyclopropane).

Preparation of 7-Chloro-7-methylbicyclo[4.1.0]hept-3-ene (117)

A dry 100 ml three-necked flask was equipped with a mechanical stirrer, addition funnel with a septum and a dry ice condenser with nitrogen inlet. 1,4-Cyclohexadiene (5 g, 0.0625 moles) and freshly distilled 1,1-dichloroethane (2.12 g, 0.0208 moles) were added to 50 ml of anhydrous diethyl ether, cooled to -40°. 2.4 M n-Butyllithium in hexane (1.11 g, 0.0714 moles) was added dropwise over the course of ten minutes while maintaining the reaction mixture at -30° to -40°. The mixture was then stirred for thirty minutes during
which time the temperature was allowed to rise to room temperature. Water was then added and the organic layer separated from the aqueous layer. The aqueous phase was back-extracted twice with ether. The ether extracts were then combined and dried over Na$_2$SO$_4$. Solvent and unreacted 1,4-cyclohexadiene were removed by distillation through a vigreux column. The remaining residue was then distilled very carefully to afford 2.15 g (86%) of 117, b. p. 69°-71°/20 mm Hg.

NMR (CHCl$_3$-d)  
0.75-2.65(m, 12 H), 1.35(s, 3H, methyl), 1.55(s, 3H, methyl), 5.45(m, 2H, vinyl), 5.65(m, 2H, vinyl).

For NMR and IR spectra of 117, see Appendix III, Figures 11a and 11b.

Elimination of 117 With Ethanolic KOH.

A 50 ml three-necked flask, equipped with a magnetic stirrer, addition funnel and reflux condenser with nitrogen inlet, was charged with (0.9942 g, 0.0158 moles) of KOH and 20 ml of ethanol. The solution was heated to 80° in an oil bath and then 7-chloro-7-methylbicyclo[4.1.0]hept-3-ene, 117, (1.5 g, 0.0105 moles) was added dropwise. The mixture was stirred at this temperature for one hour. Water was added and the product extracted into petroleum ether (20°-40°). The pet ether extracts were combined and washed with saturated brine solution. Drying (Na$_2$SO$_4$) and solvent removal yielded
0.89 g of a crude product. Further purification by distillation gave 0.78 g (70%) of 7-methylenebicyclo[4.1.0]hept-2-ene, ~\text{114}, b.p. 25\degree/0.25 mm Hg. Analytical samples were obtained by preparative glpc (20\% SE-30 on Chromosorb P column at 120\degree).
REFERENCES


42. R. West and D. C. Zecher, ibid., 89, 152 (1967).


87. Shields and Gardner (reference 19) report that the use of a stronger base but a weaker nucleophile (KOT-Bu) was essential to dehydrohalogenate in the presence of SMe.


PART II. ATTEMPTED SYNTHESIS OF ANTHRO[b]CYCLOPROPENE
INTRODUCTION

Since the initial work of Mills and Nixon\(^1\) in 1930, the possibility of double bond fixation in an otherwise aromatic molecule has fascinated both the organic and the physical chemists alike. Although the work of Mills and Nixon has been subjected to reinterpretation,\(^2\) the effect is still frequently used to denote nonequivalence of bonds in benzene resulting from annelation. Such an effect should be particularly pronounced with the highly strained 1,2-bridged system benzocyclopropene and its derivatives.\(^3\)

X-ray crystallographic data, and thus exact bond lengths, are available for two benzocyclopropenes. Carstensen-Oeser, Müller and Dürr\(^4\) have examined dimethyl-2,5-diphenylbenzocyclopropene-7,7-dicarboxylate, \(\text{I}_2\), and found the bond lengths shown in Figure 1. It is apparent from these data that some
bond localization exists; however, the striking feature is the absence of bond localization in the direction of either Kekule structure \( \overset{\sim}{\sim} \) or \( \overset{\sim}{\sim} \). The shortened 1,6-bond may result from the ester substituents at C-7, analogous to other electron withdrawing substituents which stabilize norcaradiene structures relative to cycloheptatrienes. One might also argue that the short bridging bond is shorter than it would like to be because of the strong compressing effect of the bridging group. The X-ray data for naphtho[b]cyclopropene (Figure 2) show the same anomalies, but differ from the previous case by less extreme shortening of the bridging bond.

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**Figure 2.** Bond lengths of naphtho[b]cyclopropene
The study described here has as its goal the synthesis and X-ray structural analysis of anthro[b]cyclopropene, \( \overset{8}{\sim} \), the next analogue of the linearly fused benzocyclopropenes. Resonance structures that are expected to contribute to the resonance hybrid are illustrated below.

\[ \overset{8a}{\sim} \quad \overset{8b}{\sim} \]

\[ \overset{8c}{\sim} \quad \overset{8d}{\sim} \]

The synthetic approach to be followed makes application of the base-induced elimination-isomerization sequence employed earlier by Billups and Chow in the synthesis of benzocyclopropene, \( \overset{7}{\sim} \), and naphtho[b]cyclopropene, \( \overset{5}{\sim} \), from \textit{gem}-dichlorocyclopropanes, \( \overset{2}{\sim} \) and \( \overset{4}{\sim} \), respectively.

\[ \text{CHCl}_3 \quad \overset{\text{KOT-Bu}}{\rightarrow} \quad \overset{2}{\sim} \quad \overset{\text{Cl}}{\text{Cl}} \quad \overset{\text{KOT-Bu}}{\overset{\text{DMSO}}{\rightarrow}} \quad \overset{3}{\sim} \]

\[ \text{CHCl}_3 \quad \overset{\text{KOT-Bu}}{\rightarrow} \quad \overset{4}{\sim} \quad \overset{\text{Cl}}{\text{Cl}} \quad \overset{\text{KOT-Bu}}{\overset{\text{THF}}{\rightarrow}} \quad \overset{5}{\sim} \]
RESULTS AND DISCUSSION

The synthesis of anthro[b]cyclopropene, 8, requires compound 7 as the precursor. Compound 7, in turn, is expected to be accessible by dichlorocarbene addition to 1,4-dihydroanthracene, 6. However, compound 6 is not readily available by any known methods. Therefore, we concentrated our efforts initially on the synthesis of 6.

\[ \text{Anthracene} \xrightarrow{\text{CICIC}} \text{Anthracene}^{\text{Cl}} \xrightarrow{\text{CICIC}} 8 \]

All attempts to prepare 6 from either anthracene or 9,10-dihydroanthracene proved unsuccessful. We then resolved to
investigate the possibility of a stepwise approach in building up the anthracene system through successive generation and linking of three six-membered rings. The scheme, successfully executed, is shown below.

Scheme I.

Benzyne, generated in situ by diazotization of anthranilic acid with i-amyl nitrite in methylene chloride at refluxing temperature, was reacted for three hours with freshly distilled furan to give 1,4-epoxy-1,4-dihydronaphthalene, in 76% yield, m.p. 50°-52°. Compound
9 exhibited NMR (CHCl₃-d) absorptions § 5.75 (narrow multiplet, 2H), 6.85-7.00 (multiplet, 2H) and 6.95-7.40 (multiplet, 4H).

Diels-Alder addition of 9 with 1,3-butadiene at 170°-180° for 24 hours in a sealed pressure tube gave 10, m.p. 110°-112° in 51% yield. The NMR spectrum (CHCl₃-d) of 10 showed signals at § 1.2-2.5 (multiplet, 6H), 4.9 (narrow multiplet, 2H), 5.7-6.0 (multiplet, 2H) and 6.9-7.1 (multiplet, 4H).

Dehydration of 10 was accomplished most efficiently with concentrated HCl in boiling methanolic solution. The yield of 1,4-dihydroanthracene, 6, m.p. 135°-136°, was almost quantitative. The NMR (CHCl₃-d) of compound 6 displayed absorptions at § 3.4 (narrow multiplet, 4H), 6.0 (narrow multiplet, 2H) and 7.2-7.8 (multiplet, 6H).

Addition of dichlorocarbene to compound 6 using the method of Makosza and Wawrzyniewicz gave the dichlorocarbene adduct 7 in 58% yield, m.p. 178°-180°. Compound 7 exhibited NMR (CHCl₃-d) absorptions at § 2.05 (multiplet, 2H), 2.75, 3.45 (A₂B₂, 4H) and 7.5 (multiplet, 6H).

Reaction of 7 with 10 molar equivalents of KOT-Bu in THF for 18 hours gave the ether 11 as pale yellow crystals, m.p. 139°-141°, in 38% yield, and not the desired anthro[b]-cyclopropene, 8.
When 7 was treated with 2 molar equivalents of KOt-Bu for 2 hours, then 2-chloromethylandanthracene, 12, m.p. 190°-193°, was isolated in 35% yield.
Formation of the chloride $\sim 13$ and the ether $\sim 12$ can be explained by the mechanism shown in Scheme II.

Scheme II.
Compound \( \sim \) could undergo abstraction of proton giving the anion \( \sim \) which undergoes protonation by the solvent to yield the chloride \( \sim \). Anion \( \sim \) could also form the carbene \( \sim \) by loss of Cl\( ^{\ominus} \) followed by insertion of the \( ^{\ominus} \)Ot-Bu nucleophile and subsequent protonation yielding the ether \( \sim \). It is quite conceivable that the ether \( \sim \) can be obtained from the chloride \( \sim \). This conversion was carried out by Garratt and Davalian\(^{11}\) in their approach to anthro[b]cyclopropene, \( \sim \). The chloride \( \sim \) and the ether \( \sim \) were the only products also obtained by these workers with no formation of \( \sim \).

The failure to form \( \sim \) can be accounted for by a greater degree of bond fixation in \( \sim \) (as compared to that in naphtho-[b]cyclopropene \( \sim \)). This is interpreted in terms of the increased contribution of the resonance hybrids, \( \sim \), \( \sim \) and \( \sim \), which are all of the dimethylene-cyclopropane structure. In view of the relatively high instability of dimethylene-cyclopropane itself,\(^{12}\) anthro[b]cyclopropene is also postulated to be unstable.
Nuclear Magnetic Resonance spectra were recorded on a Varian Model EM-390, XL-100 or A-56/60A spectrometers in CDCl$_3$ solution and chemical shifts are expressed in parts per million relative to Me$_4$Si. Infrared spectra were taken as CHCl$_3$ solution on a Beckmann IR-8 spectrometer. $^{13}$C Nuclear magnetic resonance spectra were recorded on a Varian Model XL-100 spectrometer. Melting points and boiling points are uncorrected. All reactions unless noted were run under an atmosphere of nitrogen.

Anthranilic acid, isoamyl nitrite and hydroquinone were obtained from Aldrich Chemical Company. 1,3-Butadiene was supplied by Matheson Company, Inc. Hexadecyltrimethylammonium bromide (cetrimide) was obtained from Eastman Organic Chemicals. Potassium tert-butoxide was supplied by Alfa Ventron Corporation. Chloroform used for the dichlorocarbene addition was spectral grade and was obtained from the Aldrich Chemical Company.

Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use.

Preparation of 1,4-Epoxy-1,4-Dihyronaphthalene (9):

A dry one-liter three-necked flask, equipped with a mechanical stirrer, reflux condenser with nitrogen inlet and additional funnel, was flushed with nitrogen. To the flask
were added freshly distilled furan (124 g, 1.8235 moles), 100 ml of pre-dried CH₂Cl₂ and isoamyl nitrite (21.36 g, 0.1824 moles). The mixture was heated to reflux and anthanilic acid (25 g, 0.1824 moles), dissolved in 200 ml of dry THF, was added dropwise over a period of three hours. The mixture was then refluxed for an additional four hours. The mixture was then transferred to a separatory funnel and washed with 15% NaOH (3 X 400 ml) to extract the i-amyl alcohol. The organic layer was separated and washed with brine. Drying (Na₂SO₄) and solvent removal by rotary evaporation gave 20.51 g (76%) of crude 9. Recrystallization from petroleum ether (20°-40°) gave 18.39 g (70%) of 9 as a yellow solid, m.p. 50°-52°.

NMR (CHCl₃-d) 5.75 (narrow multiplet, 2H), 6.85-7.00 (multiplet, 2H) and 6.95-7.40 (multiplet, 4H).

Diels-Alder Reaction of 9 with 1,3-Butadiene.

After flushing with nitrogen, a pressure tube was charged with a solution of 1,4-epoxy-1,4-dihydronaphthalene 9, (7.52 g, 0.0522 moles), in 5 ml of xylene which contained a few crystals of hydroquinone. 1,3-Butadiene (5.64 g, ca. 9 ml, 0.1045 moles) was then condensed and the pressure tube sealed tightly. The tube was then heated in an oil bath at 170°-180° for 24 hours. After cooling, the tube was opened
carefully, excess butadiene was allowed to evaporate, and
the crude product was washed from the tube with ether.
Solvent removal in vacuo afforded a black solid which was
boiled in methanol and the polymerized diene removed by
filtration. Crystallization of the product from the
filtrate yielded 5.68 g (55%) of a brown solid. Further
recrystallization from absolute ethanol gave 5.27 g (51%)
of 10 as an off-white and powdery solid, m.p. 110°-112°.

NMR (CHCl₃-d)  § 1.2-2.5 (multiplet, 6H), 4.9 (narrow
multiplet, 2H), 5.7-6.0 (multiplet, 2H)
and 6.9-7.1 (multiplet, 4H).

Dehydration of 10

To a 500 ml three-necked flask, fitted with a mechanical
stirrer, reflux condenser with nitrogen inlet and an addition
funnel, were added 10 (13 g, 0.0656 moles) and 180 ml of me-
thanol. The solution was heated to reflux and 12 M HCl (15.82
g, 36 ml, 0.4334 moles) was added dropwise over a period of
two hours. The mixture was then refluxed for 18 hours. After
cooling the reaction flask in the refrigerator for several
hours, the solid product was filtered and then washed with
cold methanol. Drying in vacuo afforded 11.72 g (99%) of a
chunky, off-white solid, m.p. 95°-105°. The crude product was
recrystallized twice from absolute ethanol to give 11.51 g
(97.5%) of pure 1,4-dihydroanthracene (6), m.p. 135°-136°.

NMR (CHCl₃-d) δ 3.4 (narrow multiplet, 4H), 6.0 (narrow multiplet, 2H) and 7.2-7.8 (multiplet, 6H).

For NMR spectra of 6, see Appendix III, Figure 12.

Dichlorocarbene Addition to 1,4-Dihydroanthracene (6).

1,4-Dihydroanthracene, 6, (9 g, 0.05 moles), cetyltrimethylammonium bromide (0.183 g, 0.5 mmole) and spectroquality chloroform (59 g, 0.5 moles) were placed in a 500 ml three-necked flask, equipped with a mechanical stirrer, reflux condenser with a drying tube and addition funnel. To this well-stirred mixture was added aqueous NaOH (40 g, 1 mole in 80 ml) over a period of one and a half hours. The reaction was then stirred at room temperature for twenty-four hours during which time the mixture turned brown. 200 ml of water was added and the mixture extracted with chloroform (2 X 300 ml). The chloroform layers were combined and washed with saturated brine and then dried over Na₂SO₄. Solvent evaporation gave a light brown solid. Recrystallization twice from ethylacetate provided 7.61 g (58%) of pure dichlorocarbene adduct 7 as white crystals, m.p. 178°-180°.

NMR (CHCl₃-d) δ 2.05 (multiplet, 2H), 2.75, 3.45 (A₂B₂, 4H) and 7.5 (multiplet, 6H).

For NMR spectra of 7, see Appendix III, Figure 13.
Reaction of 7 with KOT-Bu (10 equiv.) in THF.

A 500 ml three-necked flask, fitted with a mechanical stirrer, reflux condenser with nitrogen inlet and addition funnel, was flushed with nitrogen and then charged with KOT-Bu (4.2748 g, 0.0382 moles) and 150 ml of dry THF. To the cooled (0°) slurry was added dropwise 7 (~1 g, 3.82 moles) dissolved in 20 ml of dry THF. The reaction mixture was then stirred at room temperature for an additional 18 hours. Quenching with cold water was followed by extraction with diethyl ether. The ether extracts were combined and washed repeatedly (10x) with water and then with saturated brine. After drying over Na₂SO₄, the solvent was removed to give an orange solid, m.p. 126°-136°. Purification was achieved by sublimation to give 0.3841 g (38%) of pure ether 11 as pale yellow crystals, m.p. 139°-141°.

NMR (CHCl₃-d) § 1.37 (singlet, 9H), 4.70 (singlet, 2H),
7.45 (multiplet, 3H), 8.00 (multiplet, 4H) and 8.42 (singlet, 2H).

For NMR spectra of 11, see Appendix III, Figure 14.

Reaction of 7 with KOT-Bu (2 equiv.) in THF.

In a dry 250 ml three-necked flask, fitted with a mechanical stirrer, reflux condenser with nitrogen inlet and an addition funnel, was prepared a slurry of KOT-Bu (0.8550 g, 7.63 mmoles) in 60 ml of dry THF. Maintaining the reaction mixture at 0°, 7 (~1 g, 3.82 mmoles) dissolved in 20 ml
of dry THF was added dropwise over a period of thirty minutes. The ice bath was removed and the mixture stirred at room temperature for an additional two hours. The mixture was quenched with cold water and extracted with diethyl ether (2 X 200 ml). The extracts were combined and washed exhaustively (10 times) with H₂O and then with saturated brine. Drying (Na₂SO₄) and removal of solvent yielded a brown solid, m.p. 150°-158°. Recrystallization from ethanol gave 0.300 g (35%) of 2-chloromethylantracene, 12, as yellow crystals, m.p. 190°-193°.

NMR (CHCl₃-d) δ 4.75 (singlet, 2H), 7.40 (multiplet, 3H), 7.95 (multiplet, 4H) and 8.35 (singlet, 2H).

For NMR spectra of 12, see Appendix III, Figure 15.
REFERENCES


OTHER INVESTIGATIONS

Attached as Appendix I is a reprint describing a third study undertaken during the course of this Ph.D. work. It is entitled "Synthesis of 3-Chloro- and 3-Bromobenzocyclopropene" and has been published in *Tetrahedron Letters*. This work was done in collaboration with Mr. William T. Chamberlain.

An experimental section of this study is attached as Appendix II.
APPENDIX I. SYNTHESIS OF 3-CHLORO- AND 3-BROMOBENZOCYCLOPROPENE
SYNTHESIS OF 3-CHLORO- AND 3-BROMOBENZOCYCLOPROPENE

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It has been demonstrated that 7,7-dichlorobicyclo[4.1.0]-hept-3-enes are excellent precursors to benzocyclopropenes. We report here an application of this method to the synthesis of the functionalized benzocyclopropenes 1 and 2, potential precursors to cyclopropabenzynes 3 and 4.

The starting material 5, m.p. 77°-78° C, was prepared in 63% yield by chlorination of 7,7-dichlorobicyclo[4.1.0]hept-3-ene. The presence of seven distinct signals in the $^{13}$C NMR spectrum establishes the stereochemistry.

Reaction of 5 with KO$_2$-Bu (6 equiv.) in THF at room temperature for 18 hours gave 1 in 61% yield. Purification was achieved by bulb to bulb distillation at 0.02 mm Hg. In dimethyl sulfoxide, the yield of 1 was 45%. Spectral data for
are: NMR (d-CHCl₃) δ 3.30 (s, 2H) and 7.20 (narrow multiplet, 3H); IR (neat) 1665 cm⁻¹ (aromatic double bond);

\[ \text{C}_2\text{H}_5\text{OH} \]

UV \( \lambda_{\text{max}} \) 273 (ε=910), 278 (ε=1100), and 285 (ε=910) nm.

Since this result conflicts with the recent report of Kumar, Tayal, and Devaprabhakara,\(^6\) who reported that \( \sim \) gives 2-chlorobenzocyclopropene upon treatment with KOt-Bu in DMSO, the position of the halogen was established unequivocally by \( \sim \)

\[ \text{C} \text{NMR spectroscopy as follows: when subjected to single frequency off resonance decoupling, three of the aromatic carbons were singlets, one was a clear doublet, indicating bonding to a proton which is isolated from the other protons, and the doublets for the remaining two aromatic carbons showed extra lines due to second-order transitions resulting from bonding to adjacent coupled protons.} \]

The silver ion catalyzed methanolysis\(^7\) of \( \sim \) gave \( \sim \), identical in all respects with an authentic sample prepared by methanolysis of p-chlorobenzylbromide.
Compound 2 was prepared by treating 1 with KOT-Bu in THF or DMSO in 46% and 40% yields, respectively. Spectral data:
NMR (d-CHCl₃) δ 3.12 (s, 2H) and 6.79-7.15 (m, 3H); IR (neat) 1660 cm⁻¹; UV λmax C₂H₅OH 273 (ε=1020), 278 (ε=1190), and 285 (ε=1000). The location of the bromine was established by ¹³C NMR spectroscopy as described previously for 1.

We are currently investigating the generation of the benzynes 3 and 4.
REFERENCES


APPENDIX II
EXPERIMENTAL SECTION

Nuclear Magnetic Resonance spectra were recorded on a Varian Model EM-390, XL-100, or A-56/60A spectrometer; chemical shifts are expressed in parts per million relative to Me₄Si. Infrared spectra were taken as neat films on a Beckmann IR-8 spectrometer. Ultraviolet spectra were recorded in ethanol solution, using a Cary Model 17 spectrophotometer. ¹³C Nuclear magnetic resonance spectra were taken on a Varian Model XL-100 spectrometer. Melting points and boiling points are uncorrected.

Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. Dimethylsulfoxide was distilled from CaH₂ and stored over activated 4A molecular sieves.

Preparation of 7,7-Dichlorobicyclo[4.1.0]hept-3-ene

To a mechanically stirred mixture of 1,4-cyclohexadiene (20 g, 0.25 moles), cetrimide (0.911 g, 0.0025 moles) and chloroform (29.75 g, 20 ml, 0.25 moles) maintained at 0° by an ice bath, was added aqueous sodium hydroxide (25.3 g in 52 ml) during thirty minutes. The ice bath was removed and the
mixture allowed to warm to room temperature and stir for 24 hours. The mixture was diluted with cold water (100 ml) and extracted with chloroform (2 x 200 ml). The extracts were combined, washed with water and then with saturated NaCl solution. Drying (Na₂SO₄) and solvent removal in vacuo gave a yellow liquid, the NMR and Glpc analysis of which showed a small amount of 1,4-cyclohexadiene in addition to the expected product. Careful distillation yielded 20.5 g (50%) of 7,7-dichlorobicyclo[4.1.0]hept-3-ene, b.p. 56°-57°/1mm. The product was approximately 95% pure by gas chromatographic analysis, using a 20% SE-30 on Chromosorb P column operated at 120°.

Preparation of 3,4,7,7-Tetrachlorobicyclo[4.1.0]heptane (5)

Into a 250 ml three-necked flask, equipped with a magnetic stirrer, dry ice condenser with nitrogen inlet and a dip tube, was prepared a solution of 7,7-dichlorobicyclo[4.1.0]hept-3-ene (6 g, 0.0368 moles) and 100 ml of chloroform. Chlorine (2.62 g, 0.0368 moles), which was pre-condensed in a trap, was then allowed to boil into the solution while maintaining the reaction mixture at 0°. The mixture was then allowed to stir for an additional thirty minutes at 0°. The mixture was then washed with sodium thiosulfite, sodium bicarbonate, water and saturated brine. Drying over Na₂SO₄ and solvent removal in vacuo afforded 6.1 g (70%) of an off-white solid. Recrystallization from n-pentane gave 5.43 g (63%) of colorless and
needle-shaped crystals of 3,4,7,7-tetrachlorobicyclo[4.1.0]-heptane, δ, m.p. 77°–78°. The 13C-NMR spectrum gave seven distinct signals, establishing the trans stereo-chemistry.

Preparation of 3-Chlorobenzocyclopropene (1)

As in the case of the parent benzocyclopropene itself, 3-Chlorobenzocyclopropene also has an extremely unpleasant odor; therefore, use of a very efficiently ventilated hood is highly recommended. A 500 ml three-necked flask, equipped with a mechanical stirrer, a reflux condenser and addition funnel was flame-dried while flushing out with nitrogen. KOt-Bu (14.4 g, 0.1282 moles) and 200 ml of dry THF were added to the flask. 3,4,7,7-Tetrachlorobicyclo[4.1.0]heptane, δ, (5 g, 0.0214 moles) dissolved in 20 ml of dry THF was added dropwise to the slurry over a period of thirty minutes whilst the latter was cooled by an ice bath. The mixture was then stirred at room temperature for 18 hours. The reaction was quenched by the addition of 100 ml of chilled H$_2$O and then extracted into pentane (2 X 150 ml). The pentane extracts were combined and washed thrice with water and twice with saturated brine. Drying (Na$_2$SO$_4$) and solvent removal in vacuo afforded a black liquid. Purification was achieved by a bulb to bulb distillation at 0.02 mm
Hg which gave 1.62 g (61%) of pure 3-chlorobenzocyclopropene (1). Spectral data are as follows:

NMR (CHCl₃-d) δ 3.30 (s, 2H) and 7.20 (narrow multiplet, 3H);
IR (neat) 1665 cm⁻¹ (aromatic double bond);
UV λ<sub>max</sub><sub>EtOH</sub> 273 (ε=910), 278 (ε=1100) and 285 (ε=910) nm.

The position of the chlorine was established unequivocally by ¹³C-NMR spectroscopy.

Preparation of 3-Chlorobenzocyclopropene (1).

A 100 ml three-necked flask, equipped with a mechanical stirrer, addition funnel and nitrogen inlet, was flushed with nitrogen. To the flask was added KO₂-Bu (3.41 g, 0.0304 moles) and 40 ml of dimethyl sulfoxide.* The mixture was cooled (15°-20°) with an ice bath ** and 5 (1.78 g, 0.0076 moles) dissolved in 20 ml of dry DMSO, was added dropwise. The mixture was allowed to warm to room temperature and stirred an additional thirty minutes. The reaction was quenched by first cooling the flask and then adding 20 ml of chilled water. The product was extracted into pentane (2 X 100 ml), the extracts combined and washed with water and then with brine.

* Dimethyl sulfoxide was dried over CaH₂ and distilled immediately prior to use.

** To prevent freezing the dimethyl sulfoxide, care should be taken.
Drying (Na$_2$SO$_4$) and solvent evaporation in vacuo gave a black liquid. Bulb-to-bulb distillation at 0.02 mm Hg yielded 0.424 g (45%) of pure 3-chlorobenzocyclopropene (~).

Reaction of ~ with Silver Fluoroborate in Methanol.

To a stirred solution of 3-chlorobenzocyclopropene (~) (0.500 g, 4.1 mmoles) in 10 ml of absolute methanol cooled in an ice bath was added AgBF$_4$ (7.95 mg, 0.041 mmoles). After stirring for thirty minutes in the ice bath, saturated brine was added and the water layer extracted with petroleum ether (20°-40°) twice. The extracts were combined and dried (Na$_2$SO$_4$). Glpc analysis (20% UCON on Chromosorb P column at 160°) showed the presence of one major component and traces of dichlorodihydroanthracene and dichlorodihydrophenanthrene. The major product was characterized as methyl p-chlorobenzyl ether (~), (0.588 g, 92%).

Preparation of 7,7-Dibromobicyclo[4.1.0]hept-3-ene

In a 500 ml three-necked flask, fitted with a mechanical stirrer, addition funnel and nitrogen inlet, was prepared a slurry of KOt-Bu (9.34 g, 0.0834 moles) in 200 ml of spectroqual. pentane. 1,4-Cyclohexadiene (10 g, 0.125 moles) was
added all at once and the mixture stirred at 0°-5° for 15 minutes. Maintaining the reaction temperature at 0° to 5°, freshly distilled bromoform (21.1 g, 0.0834 moles) was added dropwise during one hour. The mixture was then allowed to warm up to room temperature and stirred for an additional three hours, during which time it turned a pale yellow color. The reaction mixture was quenched by the addition of 100 ml of chilled water, and extracted with pentane (2 x 200 ml). The pentane extracts were combined, washed twice with water, and once with saturated brine. Drying (Na₂SO₄) and solvent removal in vacuo afforded 18 g of a bright yellow liquid. Glpc analysis (20% SE-30 on Chromosorb P column at 150°) showed 87% of 7,7-dibromobicyclo[4.1.0]hept-3-ene product, and ca. 6% of 1,4-cyclohexadiene. The mixture was fractionally distilled. 1 g of 1,4-cyclohexadiene, b.p. 38°-40°/16 mm and 15.82 g (75%) of 7,7-dibromobicyclo[4.1.0]hept-3-ene, b.p. 105°-107°/16 mm., were obtained. The product showed ca. 95% purity using the same column as above at 150°.

Preparation of 3,4,7,7-Tetraphenylbicyclo[4.1.0]heptane (7)

A 250 ml three-necked flask was charged with 7,7-dibromobicyclo[4.1.0]hept-3-ene (4.6 g, 0.0184 moles) and 80 ml of freshly distilled diethyl ether. Maintaining the mixture at -5° by use of an ice-salt bath, bromine (3 g, 0.0184 moles)
was added dropwise over a course of thirty minutes. When the orange color persisted, the mixture was poured into a separation funnel and washed, first with saturated sodium thiosulfite solution, several times with H$_2$O, and finally with saturated NaCl solution. Drying (Na$_2$SO$_4$) and evaporation of solvent afforded a light yellow solid. Recrystallization from CCl$_4$ gave 4.35 g (57%) of 3,4,7,7-tetrabromobicyclo[4.1.0]heptane, white needle-shaped crystals, m.p. 98°-99°. The $^{13}$C-NMR spectrum also displayed seven distinct signals.

Preparation of 3-Bromobenzocyclopropene (2).

3-Bromobenzocyclopropene, 2, also has a very unpleasant odor. In a dry one-liter three-necked flask, fitted with a mechanical stirrer, additional funnel and nitrogen inlet, was prepared a solution of KOT-Bu (40.8 g, 0.3642 moles) in 500 ml of dry THF. To the cooled (0°) mixture was added dropwise 3,4,7,7-tetrabromobicyclo[4.1.0]heptane, 1, (25 g, 0.0607 moles) dissolved in 50 ml of dry THF. The ice bath was removed and the mixture allowed to stir at room temperature for 18 hours. The work-up was the same as above. Purification of the crude product was also done by bulb to bulb distillation at 0.03 mm Hg, affording 4.72 g (46%) of pure 3-bromobenzocyclopropene (2). Spectral data are as follows:

NMR (CHCl$_3$-d)  
S 3.12 (s, 2H) and 6.79-7.15 (m, 3H);

IR (neat)  
1660 cm$^{-1}$;

UV $^\text{EtOH}_{\text{max}}$  
273 ($\varepsilon$=1020), 278 ($\varepsilon$=1190) and 285 ($\varepsilon$=1000) nm.
The position of the bromine was established by $^{13}\text{C}-\text{NMR}$ spectroscopy as described previously for 1.

Preparation of 3-Bromobenzocyclopropene (2).

3-Bromobenzocyclopropene, 2, was prepared by treatment of 7 with KO$_2$-Bu in DMSO using the same procedure as described previously for 5. A yield of 40% was obtained.

Preparation of 3,4-Dibromo-7,7-Dichlorobicyclo[4.1.0]heptane:

A 250 ml three-necked flask, fitted with a magnetic stirrer, addition funnel and nitrogen inlet, was charged with 7,7-dichlorobicyclo[4.1.0]hept-3-ene (6 g, 0.0368 moles) and 100 ml of chloroform. Bromine (5.89 g, 0.0368 moles) was added dropwise over a period of one hour whilst maintaining the mixture at 0°. After the addition was completed, the reaction was stirred for an additional thirty minutes. Work-up was the same as above. After recrystallization from carbon tetrachloride, 9.1 g (60%) of 3,4-dibromo-7,7-dichlorobicyclo[4.1.0]heptane, m.p. 94°-95°, was obtained. The presence of seven distinct signals in the $^{13}\text{C}$-NMR spectrum also established the trans stereochemistry.
Reaction 2 with Silver Fluoroborate in Methanol:

This reaction was carried out under the conditions described above for 1. GLPC analysis (20% UCON on Chromosorb P column operated at 170°) revealed the presence of one major component and traces of dibromodihydroanthracene and dibromodihydrophenanthrene. The major component was identified as methyl p-bromobenzyl ether (0.565 g, 95%).
APPENDIX III. SPECTRA
Figure 2a

Figure 2b
Figure 9a

Figure 9b
Figure 12