INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in “sectioning” the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University Microfilms International
300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND
BUYNAK, JOHN DAVID

THE SYNTHESIS OF NOVEL AROMATIC COMPOUNDS

Rice University

University Microfilms International

300 N. Zeeb Road, Ann Arbor, MI 48106

18 Bedford Row, London WC1R 4EJ, England

Ph.D.  1980
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs ______
2. Colored illustrations ______
3. Photographs with dark background ______
4. Illustrations are poor copy ______
5. Print shows through as there is text on both sides of page ______
6. Indistinct, broken or small print on several pages ✓ throughout ______
7. Tightly bound copy with print lost in spine ______
8. Computer printout pages with indistinct print ______
9. Page(s) ______ lacking when material received, and not available from school or author ______
10. Page(s) ______ seem to be missing in numbering only as text follows ______
11. Poor carbon copy ______
12. Not original copy, several pages with blurred type ______
13. Appendix pages are poor copy ______
14. Original copy with light type ______
15. Curling and wrinkled pages ______
16. Other __________________________
RICE UNIVERSITY

THE SYNTHESIS OF
NOVEL AROMATIC COMPOUNDS

by

JOHN D. BUYNAK

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

Dr. W. E. Billups
Dr. W. E. Billups
Chairman

Paul S. Engel
Dr. Paul S. Engel

Roger L. Storck
Dr. Roger L. Storck

HOUSTON, TEXAS

MAY 1980
ACKNOWLEDGEMENTS

I would like to dedicate this thesis to my parents, Mr. and Mrs. John J. Buynak. Without their love, continual encouragement, and generous financial support, I would not have completed my graduate study. I would also like to thank Dr. W. E. Billups for his friendship and guidance. I acknowledge the financial support of Rice University, the Robert A. Welch Foundation, and the Petroleum Research Fund administered by the American Chemical Society.
ABSTRACT

The Synthesis of Novel Aromatic Compounds by John D. Buynak

2-Chloro-1,3-didehydronaphthalene was generated as a reactive intermediate in both the open (diradical) and closed (bicyclo[3.1.0]hexatriene) forms by treating either 1-bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane or 3,4-benzo-1,6,6-trichlorobicyclo[3.1.0]hexane with potassium tert-butoxide in tetrahydrofuran at 0°C. The open form reacts with solvent to produce 2-chloronaphthalene, 2-chloro-1-(2'-tetrahydrofurfuryl)naphthalene, and 2-chloro-3-(2'-tetrahydrofurfuryl)naphthalene. The closed form reacts with nucleophiles to produce 2,3-dichloronaphthalene, 2-bromo-3-chloronaphthalene, 1,2-dichloronaphthalene, 1-bromo-2-chloronaphthalene, 1,3-di(tert-butoxy)naphthalene, 1-tert-butoxy-2-chloronaphthalene, and 2-tert-butoxy-3-chloronaphthalene.

Naphtho[a]cyclopropene was generated in low yield by treating 1-bromo-2-(p-boluencesulphonatomethyl)naphthalene with n-butyl lithium in tetrahydrofuran at -15°C. This compound was characterized by both low temperature nuclear magnetic resonance spectroscopy and by its reaction with tert-butyl alcohol in the presence of silver tetrafluoroborate to produce a mixture of 1 and 2-(tert-butoxymethyl)-naphthalene.

The reactions of 2,2-dichloro-1-methylene cyclopropane with potassium tert-butoxide were studied. The products of this reaction
were cis and trans-1-tert-butoxybut-1-ene-3-yne. 2-Chloro-1-methylene-
cyclopropene is proposed as a reactive intermediate in these reactions.
# TABLE OF CONTENTS

Introduction .................................................. 1

The Generation of 1,3-Didehydronaphthalene as a Reactive Intermediate
   Background .................................................. 3
   Results and Discussion .................................... 9
   Experimental .................................................. 25
   Literature Cited ............................................. 37
   Spectra ....................................................... 38

A Synthesis of Naphtho[a]cyclopropene
   Background .................................................. 73
   Results and Discussion .................................... 77
   Experimental .................................................. 79
   Literature Cited ............................................. 82
   Spectra ....................................................... 83

Reactions of a Substituted Methylene cyclopropene
   Background .................................................. 90
   Results and Discussion .................................... 94
   Experimental .................................................. 99
   Literature Cited ............................................. 102
   Spectra ....................................................... 103

Appendix: The Reaction of Collman's Reagent with Carbon Dioxide
   Results and Discussion .................................... 114
   Experimental .................................................. 116
   Literature Cited ............................................. 117
   Spectra ....................................................... 118
   Index of Spectra ............................................. 119
Introduction

Strained aromatic systems have fascinated the synthetic organic chemist by providing him with an increased knowledge of electron delocalization and, indeed, of the nature of the chemical bond itself. Strain has been introduced in aromatic molecules in primarily three ways:

1) By the fusion of small ring systems onto the aromatic nucleus as in benzocyclopropene (1).

\[ \text{Diagram 1} \]

2) By the eclipsing and bending of the aromatic rings as in the cyclophanes (2).

\[ \text{Diagram 2} \]

3) By generating dehydroaromatics as reactive intermediates as in 1,2-dehydrobenzene or benzyne (3).

\[ \text{Diagram 3} \]
In this thesis, the generation of 4 as a reactive intermediate and the synthesis of 5 is described. Another study involving 2-substituted derivatives of methylenecyclopropene (6) is presented in the third section. An appendix describes the reaction of Collman's reagent with carbon dioxide.
The Generation
of 1,3-Didehydronaphthalene
as a Reactive Intermediate

I. Background

The most familiar of the dehydrobenzenes is 1,2-dehydrobenzene or benzyne. The chemistry of this transient species has been extensively studied and reviewed\(^1\) and it will not be further discussed here. Somewhat less familiar are the 1,3 and 1,4-dehydroaromatic systems.

Fisher and Lossing were the first to attempt to detect a 1,4-dehydrobenzene.\(^2\) They pyrolyzed 1,4-diiodobenzene in a reactor coupled to a mass spectrometer. They identified a species which has a parent ion of 76 and assigned it as 3-hexene-1,5-diyne on the basis of its ionization potential.

This was followed closely by the work of Berry, Clardy, and Schaefer\(^3\) who photolytically decomposed 1,4-benzenediazoniumcarboxylate (7). They also observed a species with a parent ion of 76 and were able to rule out 3-hexene-1,5-diyne on the basis of its UV spectrum. They point to the most likely structure as \(\text{8}\) or \(\text{9}\).

\[
\text{7} \xrightarrow{\text{hv}} \text{8} \quad \text{or} \quad \begin{array}{c}
\text{9}
\end{array}
\]
The most conclusive evidence for a 1,4-dehydrobenzene is found in the work of Bergman\textsuperscript{4} who proposed it as an intermediate in the thermal isomerization of cis-3-hexene-1,5-diyne (10). Trapping studies verified the 1,4-diradical nature of this intermediate.

By an alternate pathway, Breslow\textsuperscript{5} proposed to have generated the bicyclo[2.2.0]hexatriene, butalene (9). Butalene was prepared by treating 3-chloro[2.2.0]bicyclohexadiene (11) with lithium dimethylamide.
The most characteristic reaction of butalene is its ability to accept nucleophiles to produce substituted benzenes. It is not yet clear whether this is the result of direct addition to the strained 1,4-bond or 1,2-addition to a double bond followed by rearrangement. Homolysis of the 1,4-bond to produce Bergman's diradical intermediate does not seem to occur. The intermediate can also be trapped with the "super diene," 1,3-diphenylisobenzofuran (DPIBF).
Chapman and coworkers have recently synthesized 9,10-dehydroanthracene (13) by the photochemical decomposition of the isoketene 12. Spectroscopic evidence as well as reactivity trends seem to indicate that 13 exists as a singlet diradical.

Wong and Sondheimer7 have extended the Bergman method to the synthesis of 5,12-dihydro-6,11-didehydryronaphthacene (14). The di-lithio derivative of 1,2-diethynylbenzene was reacted with an equimolar amount of 1,2-di(p-toluenesulfinatomethyl)benzene to yield 5,12-dihydronaphthacene. When the reaction was performed in d8-THF, the isolated dihydryronaphthacene was deuterated in the 6 and 11 positions. Thus it appears that diradical 14 is a viable intermediate.

Despite considerable effort, there is not, to date, much direct evidence supporting the existence of a 1,3-dehydroaromatic. Jones and Beveridge8 proposed the existence of 2,6-dehydropyridine on theoretical grounds as early as 1964. Since then, several studies9 of the action of strong base on 2-halogenopyridines (15) have yielded only inconclusive evidence for the existence of a 2,6-dehydropyridine (16).
Berry, Clardy, and Schafer's early work\textsuperscript{10} on the flash vacuum pyrolysis of meta-diazonium carboxylate supported the existence of a product whose mass and ultraviolet spectrum were compatible with a 1,3-dehydrobenzene structure. He was not able to provide any evidence for either of the two geometrical representations 17 or 18.

Rossi and coworkers\textsuperscript{11} extended this approach to several functionalized meta-diazoniumbenzene carboxylates and claimed indirect evidence for a zwitterionic structure 19.
The most extensive study was undertaken by Washburn and coworkers. They found that treatment of exo,exo-4,6-dibromobicyclo[3.1.0]hex-2-ene (20) with base yields, among other products, 6-tert-butoxyfulvene. Labelling studies and control experiments showed that this is compatible with the intermediacy of a bicyclo[3.1.0]hexatriene (21).
II. Results and Discussion

Prior to the work of Washburn, the Billups' group had also attempted the preparation of a 1,3-dehydrobenzene via a base-induced elimination of hydrogen halide from a bicyclo[3.1.0]hexane 22 and the major product (98.4%) was chlorobenzene. This product is most likely formed via a base-induced ring opening of anion 23. A dehydrobenzene is obviously not required as an intermediate. The results of this work are well reported in D. Wolff's thesis.

As the next logical step toward forming a 1,3-dehydroaromatic, we turned our attention toward the annelated system, meta-naphthalene (24). The precursors to be used include the halocarbons 25, 26, 27, and 28.
2,3-Benz0-6,6-dichlorobicyclo[3.1.0]hexane (25) had been prepared by Parham and coworkers\textsuperscript{13} in 8% yield. Our yield, however, was increased to 57% by the micellar method of Joshi.\textsuperscript{14} Treatment of 25 with four equivalents of potassium \textit{tert}-butoxide in THF at room temperature produced, in quantitative yield, a mixture of 99.9% 2-chloronaphthalene and 0.1% naphthalene. The major product once again resulted from the base-induced ring expansion as depicted below.

\[
\begin{align*}
25 \quad & \xrightarrow{\text{KOT-Bu, THF}} \quad 99\% \quad \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \quad \quad <1\% \\
\end{align*}
\]

There exists the possibility that the minor product, naphthalene, resulted from an intermediate meta-naphthalyne diradical which abstracted hydrogen atoms from the solvent.

\[
\begin{align*}
\text{H} \quad & \xrightarrow{\text{RH}} \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\end{align*}
\]
In order to intercept the benzylic anion before the opening of the cyclopropane, a leaving group was placed at the bridgehead position. The synthesis of 1-bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26) is depicted below. 2-Bromoindene was prepared from indene via an established route in 13% yield. Micellar carbene addition produced 26 in 30% yield. Compound 26 is an unstable material decomposing to a 19:1 mixture of 2-bromo-3-chloronaphthalene and 2,3-dichloronaphthalene with a half life of 48 minutes at 40°C in DMSO. In diethyl ether, carbon tetrachloride, deuterochloroform, or tetrahydrofuran, however, there was no detectible decomposition over the course of one hour at room temperature.
When 26 was treated with four equivalents of potassium tert-butoxide in THF at 0°C, the following array of products could be isolated.

Several of the products were unequivocally identified by independent synthesis. Thus, 1-tert-butoxy-2-chloronaphthalene (35) was synthesized from 2-chloro-1-naphthol in low yield by treatment with isobutylene in the presence of a catalytic amount
of acid. 1,2-Dichloronaphthalene (32) was prepared from 2-amino-1-nitronaphthalene according to the procedure of Clemo, Cockburn, and Spence. 17 1-Bromo-2-chloronaphthalene (31) was prepared from 2-amino-1-bromonaphthalene according to the procedure of Clemo et. al. 17

Finally, the 1,3-di-tert-butoxynaphthalene (34) was cleaved to 1,3-naphthalenediol by treatment with 48% HBr in acetic acid. The other products were identified either from spectral data or by comparison
with commercially available materials.

As seen before, the 2-bromo-3-chloronaphthalene can be explained by a base-catalyzed ring expansion. The 2,3-dichloronaphthalene

![Chemical structure]

formed in the thermolysis most likely comes from disrotatory ring opening of the three membered ring with concomitant capture of the leaving chloride ion followed by elimination of HBr. This is less

![Chemical structure]

likely under basic conditions as the first step is probably formation of the benzylic anion followed by ring opening.

Several of the products, most notably 29, 37, and 38 are highly suggestive of a diradical intermediate. 2-Chloronaphthalene could have been produced by hydrogen atom abstraction from the solvent.

![Chemical structure]

\[ \text{2RH} \]
In like fashion, products 37 and 38 could be formed by hydrogen atom abstraction from the solvent followed by combination of the two remaining radicals as indicated below. Such a scheme would imply that the two radicals remain in close proximity to one another as they might in a solvent cage.

The products 1-tert-butoxy-2-chloronaphthalene (35) and 3-tert-butoxy-2-chloronaphthalene (36) result from addition of tert-butoxide at some point on the reaction pathway. It is tempting to suggest that these products result from direct addition across the strained 1,3-bond as illustrated. However, alternative pathways
cannot be ruled out. One somewhat likely possibility is transformation of the product, 2-bromo-3-chloronaphthalene (31), to a 1,2-didehydroanaphthalene followed by capture of the nucleophile.

\[ \begin{array}{c}
\text{Cl} \\
\text{Br}
\end{array} \quad ? \quad \begin{array}{c}
\text{Cl} \\
\end{array} \xrightarrow{1) \ KOT-Bu} \begin{array}{c}
\text{Cl} \\
\text{O}_{\text{t-Bu}}
\end{array} \xrightarrow{2) \ H^+} \begin{array}{c}
\text{Cl} \\
\end{array}
\]

31 36

In order to explore the possibility that a diradical intermediate is formed, the reaction was conducted in d₈-THF. Indeed, the products which would have been expected to arise from radical intermediates did contain deuterium. GC/MS analysis showed the 2-chloronaphthalene to be 79% dideuterated. The CMR is consistent with deuteration at the 1 and the 3-positions. Although carbons 1 and 3 were not clearly resolved in the spectrum due to long relaxation times, signals for carbons 4 and 9 were clearly established in the deuterated sample. These signals for the carbons adjacent to the carbons bonded to deuterium are shifted relative to the protiated material. The tabulated data is shown in Table I. The only other products to incorporate deuterium were 2-chloro-1-(2'-tetrahydrofuranylnaphthalene (37) and 2-chloro-3-(2'-tetrahydrofurfurylnaphthalene (38) which showed better than 85% incorporation.
Table I. $^{13}$Carbon Assignments of 2-Chloronaphthalene and $d_2$-2-Chloronaphthalene

<table>
<thead>
<tr>
<th>Carbon</th>
<th>2-Chloronaphthalene</th>
<th>$1,3$-Dideuteronaphthalene</th>
<th>Δ Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>126.50$^a$</td>
<td>126.50$^a$</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>131.15</td>
<td>131.15</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>126.50$^a$</td>
<td>126.50$^a$</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>129.50</td>
<td>129.72</td>
<td>-0.17</td>
</tr>
<tr>
<td>5</td>
<td>127.85</td>
<td>127.85</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>126.40</td>
<td>126.40</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>127.15$^b$</td>
<td>127.15$^b$</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>127.15$^b$</td>
<td>127.15$^b$</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>134.20</td>
<td>134.13</td>
<td>-0.07</td>
</tr>
<tr>
<td>10</td>
<td>131.85</td>
<td>131.85</td>
<td>0.0</td>
</tr>
</tbody>
</table>

All of the above spectra were recorded on a Varian XL-100 spectrometer at 25.2 MHz. The solvent was $d_6$-acetone. The chemical shifts are in ppm downfield from TMS; the approximate error is ±0.05 ppm.

a) Carbons 1 and 3 were not resolved from one another
b) Carbons 7 and 8 were not resolved from one another
of eight deuterium atoms.

Both to test the ability of the products to exchange deuterium with the solvent and to check their stability to the formation of 1,2-didehydroanaphthalenes, the following control experiment was performed. A mixture of non-deuterated 2-chloronaphthalene, 2,3-dichloronaphthalene, and 2-bromo-3-chloronaphthalene was subjected to the reaction conditions in $d_8$-THF as shown below. The result was

\[
\begin{align*}
\text{29} & \quad + \quad \text{30} & \quad + \quad \text{31} & \quad \xrightarrow{\text{KOT-Bu}} \quad \text{d}_8\text{-THF} \\
\end{align*}
\]

that the starting reaction mixture was quantitatively recovered in its original proportions with no detectable incorporation of deuterium. The deuterated chloronaphthalene was therefore not simply the result of a product's exchanging deuterium with the solvent. Also, it appears unlikely that the products are further transformed into 1,2-didehydroanaphthalenes by the reaction conditions.

Several other experiments were performed to further clarify the reaction mechanism. The reaction temperature was lowered to $-78^\circ C$ with no noticeable change in product composition. To determine the effect of an external nucleophile, excess dimethylamine was added to the reaction mixture. The result is shown below.

There is a noticeable absence of products resulting from free radical type reactions and a large proportion of products resulting from addition of dimethylamine. This, in fact, suggests that an intermediate is being formed which is either: 1) being trapped by a nucleophile, or 2) undergoing radical type reactions. There is, in
fact, a reasonable amount of evidence to suggest that meta-naphthalyne exhibits this dichotomy of behavior as indicated. There also exists the possibility that formation of 1,2-didehydronaphthalene (ortho-naphthalyne) might be concerted with the destruction of meta-naphthalyne thus accounting for the formation of 1,3-di(tert-butoxy)naphthalene as shown below.
In order to prepare the parent unsubstituted meta-naphthalyne, it is necessary that one of the 7,7-\textit{gem}-dichlorides be reduced. Unfortunately, all attempts at such a reduction of 26 failed. This appeared to be caused by the lability of the bridgehead bromide to reduction. In an effort to produce an alternative precursor to meta-naphthalyne, 3,4-benzo-1,6,6-trichlorobicyclo[3.1.0]hexane (27) was prepared as illustrated.

On treatment with potassium tert-butoxide in THF, the trichloride yielded products exactly analogous to that of 1-bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26). When $d_8$-THF is used as the reaction solvent, the anticipated products, 29, 37, and 38, incorporate deuterium.
As an additional test for the intermediacy of free radicals, the reaction was performed in the presence of excess 1,4-cyclohexadiene. The results are as indicated. The expected products...
and 41 are formed only in trace (<1%) amounts. 5% of the isolated material consisted of 2-chloro-3-phenylnaphthalene. This product presumably formed by oxidation of 40. The origin of 2-phenylnaphthalene, formed in trace amounts, remains a mystery.

Reduction of the thermally unstable trichloride 27 gave a crude, inseparable mixture of products under most conditions. However, when treated with ten equivalents of lithium aluminum hydride in ether at 5°C for three days, 27 gave 1,6-dichloro-3,4-benzobicyclo[3.1.0]hexane (43) in 78% crude yield. Close inspection of the spectral data seems to indicate that the stereochemistry is as shown above. All attempts to purify 43 resulted in partial or total decomposition of this extremely sensitive material. Thermolysis of crude 43 produced an 85:15 mixture of 2-chloronaphthalene and naphthalene respectively. This would seem to indicate that 43 is contaminated with some over-reduced 7-chloro-3,4-benzobicyclo[3.1.0]hexane (44) which is transformed to naphthalene on thermolysis.
Treatment of dichloride 43 with potassium tert-butoxide in THF yielded naphthalene and 2-chloronaphthalene. In order to determine whether the naphthalene had come from a 1,3-didehydrodronaphthalene or from the simple ring opening of the monochloride 44, the reaction was performed in d$_8$-THF. The recovered naphthalene showed no incorporation of deuterium indicating that it had, in fact, resulted from 44.

In conclusion, it seems fair to state that 2-chloro-1,3-didehydrodronaphthalene (45) has been synthesized as a reactive intermediate. Fragmentation of the 1,3-bond can occur by homolysis (radical) or by nucleophilic addition (ionic) pathways. The reaction conditions can be altered to favor either fragmentation pathway. The synthesis of the unsubstituted meta-naphthalene (4), however, was a failure due to unwanted ring opening reactions.

In view of the relative inaccessibility of 2,3-disubstituted naphthalenes, as well as the ease with which the 3,4-benzobicyclo-[3.1.0]hexane ring system can be opened to such naphthalenes, we
decided that it was appropriate to exploit this process. Thus, in an effort to optimize the yield of the 2,3-dihalonaphthalenes, the dichlorocarbene addition reactions of 2-bromo and 2-chloronaphthalene were performed in refluxing chloroform. The results are shown below.

\[ \text{CHCl}_3/\text{NaOH} \]

\[ \text{Br} \quad \text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_3\text{Br} \quad \Delta \quad \text{Cl} \quad + \quad \text{Cl} \quad 43\% \quad 2\% \]

\[ \text{CHCl}_3/\text{NaOH} \]

\[ \text{Cl} \quad \text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_3\text{Br} \quad \Delta \quad \text{Cl} \quad \text{Cl} \quad 60\% \]

This process represents the best synthesis to date of these dihalonaphthalenes. There exists the possibility that this scheme could be extended to produce other substituted naphthalenes.
III. Experimental

2,3-Benzoyl-6,6-dichlorobicyclo[3.1.0]hexane (25). Compound 25 was prepared by the Joshi$^{14}$ modification of the micellar carbene additions of Parham and coworkers.$^{13}$ A solution of sodium hydroxide (61.4 g, 1.53 mol) in 100 mL water was added to a solution of indene (23.2 g, 0.20 mol), hexadecyltrimethylammonium bromide (0.528 g, 1.40 mol) and alcohol-free chloroform (50 mL, 0.63 mol) dropwise with ice bath cooling. The reaction was stirred overnight at room temperature. After acidifying the reaction mixture with 10% sulfuric acid, the product was extracted into ether and washed repeatedly with water. The solution was then dried over MgSO$_4$ and concentrated in vacuo at room temperature. The product was taken up in petroleum ether and filtered through a pad of alumina. Low temperature recrystallization from petroleum ether afforded 13.2 g (57% yield) of 25.

Note: This compound had been previously prepared by Parham, Reiff, and Swartzentruber$^{13}$ in 8.0% yield. NMR (CDCl$_3$) $\delta$ 2.30-2.50 (m, 1H), 3.00-3.20 (m, 3H), 6.80-7.20 (m, 4H).

1,2-Dibromoindane. This compound was prepared according to the procedure of Weinstein and Roberts.$^{15}$ Thus, bromine (73 mL, 1.34 mol) was added dropwise to a stirred solution of freshly distilled indene (150 g, 1.29 mol) in 650 mL diethyl ether while maintaining the temperature between 0º and -5ºC. The reaction mixture was then extracted twice with a saturated solution of sodium thiosulfate, twice with water, once with brine and dried over MgSO$_4$. Removal of the solvent in vacuo afforded crude 1,2-dibromoindane of suitable
purity for dehydrobromination. Vacuum distillation afforded 310 g (87% yield) of 1,2-dibromoindane, bp 115-120°C (1.5 mm Hg).

2-Bromoindene. A solution of crude dibromoindane (400 g, 1.45 mol) was refluxed with 500 mL freshly distilled, dry tetralin for 8 hours. There was considerable HBr evolution. Fractional distillation of the reaction mixture provided 2-bromoindene, bp 77°C (1.5 mm Hg), which was further recrystallized from anhydrous methanol to yield 33.0 g 2-bromoindene (15% yield) as a white solid, mp 38°C.

1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26). This material was prepared by a modification of the micellar carbene additions of Joshi, Singh, and Pande. 14 A solution of NaOH (37.0 g, 0.925 mol) in 75 mL H₂O was added dropwise to a chilled (ice bath) solution of bromoindene (11.9 g, 61.0 mol) and hexadecyltrimethylammonium bromide (0.226 g, 0.620 mol) in alcohol-free chloroform (61.0 mL, 0.76 mol). The reaction was stirred vigorously at room temperature for approximately eight hours. Then the chloroform layer was washed several times with ice water and dried over Na₂SO₄. Evaporation of the chloroform at 0°C in vacuo yielded a brown sludge. This material was dissolved in cold petroleum ether and filtered through a pad of florisil. Evaporation of the petroleum ether at 0°C in vacuo yielded 5.2 g (30% yield) of a white solid. Although the high resolution mass spectrum showed no parent ion, the largest fragment was consistent with the loss of chlorine atom: 239.9334, calcd. for C₁₀H₇ClBr 239.9340. ¹³C NMR (CDCl₃) δ 45.90, 46.19, 50.02, 68.33, 123.59, 125.09, 126.74, 128.00, 138.07, 142.62.
Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 26 (1.00 g, 3.67 mmol) in 5 mL THF was added dropwise to a slurry of potassium tert-butoxide (1.63 g, 14.7 mmol) in 15 mL THF. The reaction was allowed to stir at 0°C for 30 minutes, then diluted with water and extracted into ether three times. The combined ether layers were washed several times with water and dried over Na₂SO₄. The solution was then concentrated in vacuo to yield 0.7 g brown solid (83% recovery). From this solid the isolated products were separated by a combination of preparative thin layer chromatography (silica gel, several solvents) and preparative gas chromatography (6'x1/4" 10% SE-30 on Chrom WAW). 1-tert-Butoxy-2-chloronaphthalene (35) has an exact mass of 234.0814 (calcd. for C₁₄H₁₅ClO: 234.0811) and ¹³C NMR (CDCl₃) δ 29.8, 78.2, 123.7, 124.2, 125.73, 125.78, 127.5, 127.6, 132.1, 133.2, 148.7. 2-tert-Butoxy-3-chloronaphthalene has an exact mass of 234.0803 (calcd. for C₁₄H₁₅ClO: 234.0811) and ¹³C NMR (CDCl₃) δ 28.8(q), 81.4(s), 120.1(d), 125.1(d), 126.0(d), 126.4(d), 126.8(d), 128.3(d), 129.2(s), 130.1(s), 132.4(s), 149.6(s).

The mixture of 2-chloro-1-(2'-tetrahydrofurfuryl)naphthalene (37) and 2-chloro-3-(2'-tetrahydrofurfuryl)naphthalene (38) was shown to be a 44:56 mixture respectively by gc using a 250 ft SF-96 capillary column and the mixture was shown to have an exact mass of 232.0666 (calcd. for C₁₄H₁₃ClO: 232.0655).

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26) with Potassium tert-Butoxide in d₈-Tetrahydrofuran. A solution of 26 (7.70 mg, 0.0277 mmol) in 0.5 g d₈-THF was added dropwise to
a slurry of potassium tert-butoxide (1.25 mg, 0.0111 mmol) in 1.5 g d$_8$-THF while cooling with an ice bath. The reaction was allowed to stir at 0°C for 30 minutes, then diluted with water and extracted into ether three times. The combined ether layers were washed several times with water and dried over Na$_2$SO$_4$. The solution was then concentrated in vacuo to yield 4.0 mg (63% recovery) brown solid. Analysis by gc/ms (3'X1/8" SE-30 on Chrom WAW) showed deuterium incorporation into 2-chloronaphthalene with 79% having two deuterium atoms, 13% having one deuterium, and 8% having no deuterium. The only other product observed to incorporate deuterium was the mixture of 2-chloro-1-(2'-tetrahydrofurfuryl)naphthalene (37) and 2-chloro-3-(2'-tetrahydrofurfuryl)naphthalene (38) which did not separate on this column but showed better than 85% incorporation of eight deuterium atoms. The $^{13}$C NMR spectrum of 2-chloronaphthalene which is partially deuterated in the 1 and 3 positions is consistent with that of perprotio-2-chloronaphthalene except for the appearance of two new signals at 129.72 ppm and 134.13 ppm due to C-4 and C-9 of the dideuterated naphthalene respectively. The long relaxation times of C-1 and C-3 in the dideuterated compound preclude their direct observation.  

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26) with Potassium tert-Butoxide in Tetrahydrofuran at -78°C. A solution of 26 (0.100 g, 0.360 mmol) in 1 mL of THF was added to a slurry of potassium tert-butoxide (0.20 g, 1.78 mmol) in 1 mL THF at -78°C. The reaction was stirred at -78°C for three hours then poured into ice water. The products were extracted several times
with ether and the ethereal layers washed with water. The ethereal
solution was then dried (NaSO₄) and concentrated in vacuo to yield
0.070 g (83% recovery) crude brown solid. Careful analysis revealed
the product mixture to be identical with that obtained in the 0°
experiment.

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane
(26) with Potassium tert-Butoxide in THF in the Presence of Dimethyl-
amine. Dimethylamine (2.7 mL, 40.8 mmol) was added to a slurry of
potassium tert-butoxide (2.0 g, 18.0 mmol) in 15 mL THF while main-
taining the bath temperature at -78°C. Then a solution of 26 (1.00 g,
3.60 mmol) in 5 mL THF was added over the course of 10 minutes. The
reaction was stirred at -78°C for one hour, then diluted with water
and extracted several times with ether. The combined ethereal layers
were washed several times with water and dried over Na₂SO₄. Concen-
tration of the solution in vacuo yielded 0.7 g brown solid (93% re-
covery) which was analyzed by gc/ms (3''X1/8'' SE-30 on Chrom WAW).
The products were purified using preparative thin layer chromatography
(silica gel, variety of solvents). 1,3-bis(dimethylamino)naphthalene
had an exact mass of 214.1480 (calcd. for C₁₄H₁₈N₂: 214.1470) and
a ¹³C NMR (CDCl₃) δ 40.9, 45.0, 102.3, 122.3, 123.6, 125.9, 126.6,
135.9, 148.4, and 151.2. 1-Dimethylamino-2-chloronaphthalene had
an exact mass of 205.0657 (calcd. for C₁₂H₁₂ClN: 205.0658) and a
¹³C NMR (CDCl₃) δ 42.6, 124.3, 125.8, 126.1, 126.3, 127.6, 128.2,
130.1, 133.0, 133.6, 145.0. 3-Dimethylamino-2-chloronaphthalene
had an exact mass of 205.0646 (calcd. for C₁₂H₁₂ClN: 205.0658) and
¹³C NMR δ 44.0, 116.3, 124.6, 126.0, 126.2, 126.4, 128.4, 128.8,
129.7, 132.5, and 148.0.
Thermolysis of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]-
hexane (26) in d₆-Dimethylsulfoxide. Compound 26 was heated in
excess d₆-DMSO for several hours. The reaction was quantitative
producing 2-bromo-3-chloronaphthalene and 2,3-dichloronaphthalene
in a ratio of 19:1 respectively. The reaction had a half-life of
48 minutes at 40°C as monitored by ¹H NMR. The temperature stability
of 26 was checked in the following solvents: THF, Et₂O, CCl₄, and
CDCl₃. After one hour at room temperature, no appreciable decompo-
sition had occurred in any of the aforementioned solvents.

Treatment of 2-Chloronaphthalene (29), 2,3-Dichloronaphthalene
(30), and 2-Bromo-3-chloronaphthalene (31) with Potassium tert-
Butoxide in d₈-THF. A mixture of halonaphthalenes 29, 30, and 31
(0.0769 g, in a ratio of 3:16:81 respectively) was added to a slurry
of potassium tert-butoxide (0.125 g, 1.11 mmole) in 1.0 g d₈-THF
while cooling with an ice bath. The reaction was allowed to warm
to room temperature over the course of one hour, then diluted with
water and extracted with ether. The combined ethereal layers were
washed several times with water then dried over MgSO₄. The solvent
was removed in vacuo to yield quantitative recovery of the halonaph-
thalenes in their original proportions with no incorporation of
deuterium.

1,2-Dichloronaphthalene (32). 1,2-Dichloronaphthalene was
prepared from 1-nitro-2-aminonaphthalene according to the procedure
of Clemo, Cockburn, and Spence. 17 2-Amino-1-nitronaphthalene (1.0 g,
5.31 mmol) in concentrated HCl (5 mL) was stirred and 20 g ice added,
followed by sodium nitrite (0.403 g, 5.84 mmol). After one hour of
stirring, the liquid was filtered and added to a solution of cuprous
chloride (3.0 g, 30.3 mmol) in HCl (8 mL) and left overnight. Dilution with water and ether extraction yielded a solid which was further purified by TLC (silica gel, petroleum ether) to yield 0.400 g (38% yield) of 1,2-dichloronaphthalene, mp 35°C.

1-Bromo-2-chloronaphthalene (33). 1-Bromo-2-chloronaphthalene was prepared from 2-amino-1-bromonaphthalene 18 according to the procedure of Clemo, Cockburn, and Spence. 17 2-Amino-1-bromonaphthalene (1.0 g, 4.50 mmol) suspended in HCl (8.0 mL) was treated with sodium nitrite (0.345 g, 5.0 mmol) and the solution added to cuprous chloride (3.0 g, 30.3 mmol) in 8 mL HCl. The solution was allowed to stir overnight and then poured into water. After extraction with ether and drying (MgSO₄), the solution was concentrated to yield a yellow solid. The solid was further purified by preparative TLC (silica gel, pentane) to yield 0.43 g (40% yield) 1-bromo-2-chloronaphthalene, mp 46°C.

1-tert-Butoxy-2-chloronaphthalene (35). 2-Chloro-1-naphthol 16 (1.24 g, 7.63 mmol) was added to a solution of sulfuric acid (0.04 mL, 0.72 mmol) in isobutylene (5.0 mL, 53.0 mmol) at -78°C in a Diels-Alder tube. The tube was capped and the solution allowed to stir at room temperature overnight. Then the slurry was cooled to -78°C and poured into 10% NaOH. The product was extracted with ether several times and the ethereal solution washed three times with 10% NaOH, once with water, and dried over MgSO₄. The ether was removed in vacuo and the product further purified by preparative thin layer chromatography (silica gel, 1 acetone:20 pentane) to yield 0.163 g pure 35 (9% yield).
Reaction of 1,3-Di(tert-butoxy)naphthalene with acid. 48% HBr (5 drops, 1.1 mmol) was added to a solution of 34 (43.7 mg, 0.160 mmol) in 3 mL glacial acetic acid. The reaction was allowed to stir at room temperature for 30 minutes, diluted with water, and extracted with ether. The ethereal solution was washed several times with water, once with brine and dried over Na₂SO₄. Evaporation of the solvent in vacuo yielded 22.4 mg (87% crude yield) of an orange oil which could be further purified by preparative thin layer chromatography (silica gel, CH₂Cl₂). The ¹H NMR of the purified product proved to be identical with that of a commercial sample (Aldrich) of 1,3-dihydroxynaphthalene.

1,2-Dichloroindane. 1,2-Dichloroindane was prepared according to the procedure of Braude and Evans.¹⁹ Thus dry chlorine was bubbled into a solution of indene (156 g, 1.34 mol) in CCl₄ (400 mL) while cooling with an ice bath. The reaction was monitored by gc (10% SE-30 on Chrom WAW), and the addition of chlorine was stopped as soon as the indene was completely reacted. The solvent and excess chlorine were removed in vacuo to yield crude material suitable for use in dehydrochlorination. The material could be distilled to yield 185 g (74% yield) of 1,2-dichloroindane, bp 86-90°C (2 mm Hg).

2-Chloroindene. Crude 1,2-dichloroindane (185 g, 0.99 mol) was heated for five hours at 225-235°C. The resulting solution was fractionally distilled at reduced pressure to yield 2-chloroindene (100 g, 67% yield) bp 110-116°C (13 mm Hg).

3,4-Benzoyl-1,6,6-trichlorobicyclo[3.1.0]hexane (27). A solution of NaOH (40 g, 1.0 mol) in 80 mL water was added dropwise to a solution
of chloroindene (10.0 g, 0.664 mol) and hexadecyltrimethylammonium bromide (0.246 g, 0.675 mmol) in CHCl₃ (66 mL, 0.82 mol) at 0°C. The reaction was warmed to 15°C and allowed to stir vigorously at this temperature for eight hours. The reaction mixture was then washed three times with ice water and dried over Na₂SO₄. The chloroform solution was then concentrated in vacuo at 0°C to yield a brown solid. This solid was then taken up in cold petroleum ether and filtered through a pad of florisil. This solution was concentrated in vacuo to yield 3.33 g (21.5% yield) of a white solid, mp 74°C. The exact mass was 231.9604 (calcd for C₁₀H₇Cl₃: 231.9613).

Reaction of 3,4-Benzol₁,6,6-trichlorobicyclo[3.1.0]hexane (27) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 27 (0.500 g, 2.08 mmol) in 3 mL THF was added to a slurry of potassium tert-butoxide (1.17 g, 10.4 mmol) in 14 mL THF while cooling with an ice bath. The reaction was allowed to stir at 0°C for 30 minutes then diluted with water and extracted three times with ether. The combined ethereal layers were washed several times with water and dried over Na₂SO₄. The solution was then concentrated in vacuo to yield 0.36 g (84% recovery) brown solid. The products were identified by gc/ms (4'x1/8" 10% SE-30 on Chrom WAW) and by comparison with authentic samples.

Reaction of 3,4-Benzol₁,6,6-trichlorobicyclo[3.1.0]hexane (27) with Potassium tert-Butoxide in d₈-THF. A solution of 27 (0.033 g, 0.137 mmol) in 0.5 mL d₈-THF was added to a slurry of potassium tert-butoxide (0.0923 g, 0.823 mmol) in 1 mL d₈-THF while cooling with an ice bath. The reaction was allowed to stir at 0°C for 30 minutes, then diluted with water and extracted three times with ether
and dried over Na₂SO₄. The solution was then concentrated in vacuo to yield 0.020 g (71% recovery) brown solid. The 2-chloronaphthalene was 10.7% dideuterated, 54.7% monodeuterated, and 34.6% nondeuterated. The mixture of 1 and 3-(2'-tetrahydrofurfuryl)-2-chloronaphthalenes was 47% d₈, 32% d₇, and 21% d₆.

3,4-Benzol-1,6-dichlorobicyclo[3.1.0]hexane (43). LiAlH₄ (1.07 g, 28.2 mmol) was cautiously added to a solution of 27 (2.63 g, 11.3 mmol) in 50 mL anhydrous ether at 0°C. The reaction was allowed to stir at 5°C for three days. The reaction mixture was then carefully poured into ice water and extracted several times with cold petroleum ether. The combined organics were then washed several times with ice water and dried over Na₂SO₄. Concentration in vacuo yielded 1.74 g (78% yield) of a yellow oil. All attempts at further purification of this material resulted in its decomposition. The exact mass was 201.9944 (calcd. for C₁₀H₈Cl₂: 201.9937).

Reaction of 3,4-Benzol-1,6-dichlorobicyclo[3.1.0]hexane (43) with Potassium tert-Butoxide in Tetrahydrofuran. A solution of 43 (1.58 g, 7.94 mmol) in 7 mL THF was added to a slurry of potassium tert-butoxide (4.45 g, 39.7 mmol) in 38 mL THF at 0°C. The reaction was allowed to stir for 30 minutes then diluted with water and extracted three times with ether. The combined ether layers were washed three times with water and dried over Na₂SO₄. The solution was then concentrated in vacuo to yield 0.90 g (75% recovery) crude product. The products were isolated and identified by a combination of gc/ms and thin layer chromatography (silica gel, variety of solvents).
Thermolysis of 3,4-Benzo-1,6-dichlorobicyclo[3.1.0]hexane (43).

A solution of 10% 43 in CDCl$_3$ was injected into a glc column (10% SE-30 on Chrom WAW) with the injection ports set at 250°C. The products were identified by mass spectroscopy.

Reaction of 3,4-Benzo-1,6,6-trichlorobicyclo[3.1.0]hexane (27) with Potassium tert-Butoxide in THF in the Presence of 1,4-Cyclohexadiene. 1,4-Cyclohexadiene (2.0 mL, 21.1 mmol) was added to a slurry of potassium tert-butoxide in 15 mL THF. The resulting mixture was chilled to 0°C and a solution of 27 (0.500 g, 2.08 mmol) in 2 mL THF was added dropwise. The reaction mixture was allowed to warm to room temperature over the course of one hour. The reaction was then diluted with water and extracted three times with ether. The combined ethereal layers were washed several times with water and dried over Na$_2$SO$_4$. Concentration of this solution in vacuo yielded 0.340 g crude material (86% recovery). The material was further purified by preparative thin layer chromatography (silica gel, variety of solvents). The mixture of 2-chloro-1-phenynaphthalene and 2-chloro-3-phenynaphthalene had an exact mass of 238.0549 (calcd. for C$_{16}$H$_{11}$Cl: 238.0549).

2,3-Dichloronaphthalene. A solution of sodium hydroxide (6.65 g, 166. mmol) in 12.3 mL water was added to a solution of chloroindene (1.54 g, 10.25 mmol) and hexadecyltrimethylammonium bromide (0.038 g, 0.104 mmol) in 10.4 mL chloroform. The reaction mixture was then heated to reflux with rapid stirring for one hour. Another 5 mL of chloroform was then added. The reaction was allowed to reflux for an additional three hours, then poured into 300 mL water and extracted three times with CH$_2$Cl$_2$. The combined organics were then washed with
water (3x) and dried (MgSO₄). Concentration in vacuo yielded a black solid which was redissolved in 300 mL petroleum ether and filtered through a pad of silica gel. The resulting solution was then concentrated in vacuo to yield 1.17 g (60% yield) of 2,3-dichloronaphthalene.

2-Bromo-3-chloronaphthalene. A solution of NaOH (6.67 g, 0.167 mmol) in 12 mL water was added to a solution of 2-bromoindene (2.0 g, 10.25 mmol) and hexadecyltrimethylammonium bromide (0.038 g, 0.104 mmol) in 10.4 mL spectroquality chloroform while heating to 45°C. The addition took place over the course of 20 minutes. The reaction was then allowed to stir at high speed for 2 hours while maintaining a bath temperature of 65°C. At this time an additional 5 mL of chloroform was added and the reaction allowed to stir for an additional 7 hours at 65°C. Then the reaction mixture was poured into 250 mL water and extracted (3x) with ether. The combined ether-eal layers were washed three times with water and once with brine. After drying (MgSO₄), the solvent was evaporated in vacuo to yield a brownish solid. The product was further purified by dissolving it in petroleum ether and filtering the solution through a small column of silica gel. Concentration of this solution in vacuo yielded 1.16 g (45% yield) white solid which proved to be a 19:1 mixture of 2-bromo-3-chloronaphthalene and 2,3-dichloronaphthalene respectively.
References


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lock Pos.</td>
<td>0.00 ppm</td>
</tr>
<tr>
<td>Lock Power</td>
<td>0.04 mG</td>
</tr>
<tr>
<td>Decouple Pos.</td>
<td>0.04 ppm</td>
</tr>
<tr>
<td>Decoupling Power</td>
<td>0.04 mG</td>
</tr>
<tr>
<td>Spectrum Ampl.</td>
<td>2000</td>
</tr>
<tr>
<td>Sweep Time</td>
<td>5 min</td>
</tr>
<tr>
<td>Nucleus</td>
<td>Hz</td>
</tr>
<tr>
<td>Sample</td>
<td></td>
</tr>
<tr>
<td>Filter</td>
<td>0.05 s</td>
</tr>
<tr>
<td>Sweep Width</td>
<td>1.0 ppm</td>
</tr>
<tr>
<td>Zero Ref.</td>
<td>90°</td>
</tr>
<tr>
<td>RF Power</td>
<td>0.04 mG</td>
</tr>
<tr>
<td>End of Sweep</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>Sample Temp.</td>
<td>Ambient ±5°C</td>
</tr>
<tr>
<td>Solvent</td>
<td>OCl₂</td>
</tr>
</tbody>
</table>
LOCK POS. ______ ppm  SPECTRUM AMP. ______  SWEEP TIME ______ min NUCLEUS ______ SAMPLE:

LOCK POWER ______ mG
DECOUPLE POS. ______ ppm
DECOUPLING POWER ______ mG
RF POWER ______ mG
END OF SLEEP ______ ppm
SAMPLE TEMP. ______°C
SOLVENT: ______
A Synthesis of
Naphtho[a]cyclopropene

I. Background

Although naphtho[b]cyclopropene (2) can be synthesized by various methods, most notably the base-induced dehydrohalogenation of 3,4-benzo-7,7-dichlorobicyclo[4.1.0]heptane (1), its isomer, naphtho[a]cyclopropene (3) had, until recently, refused to yield to the synthetic chemist.\(^1\),\(^2\) This was unfortunate in view of its potential to warrant interest in terms of bond delocalization. The

\[
\begin{align*}
1 & \xrightarrow{\text{KOT-Bu, THF}} 2 \\
\end{align*}
\]

first synthesis of naphtho[a]cyclopropene appeared in 1976 in an article by Vogel and coworkers.\(^3\) Vogel used an ingenious retro Diels-Alder reaction to generate naphtho[a]cyclopropene. Thus, 2-bromo-1,6-methano[10]annulene (4) and N,N-diethyl-1,3-butadienylamine were heated together with an excess of potassium tert-butoxide in toluene to produce 2,3-benzo-1,6-methano[10]annulene (5) in 20% yield. Reaction of 5 with dimethylacetylenedicarboxylate produces the expected Diels-Alder adduct 6. Pyrolysis of 6 at 450°C at 0.01 torr yields naphtho[a]cyclopropene in 83% yield.
Before and during the work of Vogel, attempts to synthesize naphtho[a]cyclopropene were being made in the Billups lab. The first, and perhaps most naive, synthesis was simple dehydrohalogenation of 1,2-benzo-7,7-dichlorobicyclo[4.1.0]heptane (7). Instead of yielding naphtho[a]cyclopropene however, a crude mixture of approximately 25 volatile products was obtained, the three major constituents of which are illustrated. This failure is probably due to initial elimination of HCl forming 8 which is unable to isomerize without forming the antiaromatic ion 9.
The other process which has been tried in our labs employed the Radlick\(^4\) method of benzocyclopropene synthesis. The precursor, 1-bromo-2-(methoxymethyl)naphthalene (10) was synthesized as outlined below. When 10 was treated with \(n\)-BuLi in THF as described by Radlick and Crawford,\(^4\) no naphtho[a]cyclopropene could be isolated.
II. Results and Discussion

In an effort to improve upon the Radlick method, a better leaving group than methoxy was employed at the 6-methyl position. 1-Bromo-2-(hydroxymethyl)naphthalene (12) was easily synthesized from the dibromide 11 by simple treatment with water in acetone.

\[
\begin{align*}
&\text{Br} & \text{CH}_2\text{Br} & \text{H}_2\text{O} & \text{Acetone} & \text{Br} & \text{CH}_2\text{OH} & \text{Ts-Cl} & \text{pyridine} & \text{Br} & \text{CH}_2\text{OtS} \\
&\text{11} & & & & \text{12} & & \text{13} \\
\end{align*}
\]

However, several attempts to prepare the tosylate 13 from this alcohol under increasingly forcing conditions all proved unsuccessful. The reason for this is uncertain, but it may simply be due to steric hindrance in 12.

Thus a method of tosylate synthesis known to be useful in the synthesis of hindered tosylates was employed. 1-Bromo-2-(hydroxymethyl)naphthalene (12) was reacted with p-toluenesulfinyl chloride and the resulting sulfinate oxidized as illustrated. Treatment of

\[
\begin{align*}
&\text{Br} & \text{CH}_2\text{OH} & \text{p-tolylSOCl} & \text{Br} & \text{CH}_2\text{OSO-p-tolyl} \\
&\text{12} & & & \text{13} & \\
\end{align*}
\]

\[
\begin{align*}
&\text{Br} & \text{CH}_2\text{OSO-p-tolyl} & \text{MCPBA} & \text{Br} & \text{CH}_2\text{OSO}_2\text{-p-tolyl} \\
&\text{13} & & & & \\
\end{align*}
\]
this tosylate with n-BuLi at -20°C then produced naphtho[a]cyclo-
propene in low (~4%) yield. The product was not isolated in pure
form because of its lability but was detected by low temperature
$^1$H NMR. Further evidence for the production of 3 comes from the
treatment of the crude product with silver tetrafluoroborate in the
presence of tert-butyl alcohol to produce the tert-butyl ethers 14
and 15 in a ratio of 5 to 3 respectively.
III. Experimental

1-Bromo-2-(hydroxymethyl)naphthalene (12). 1-Bromo-2-(bromo-
methylnaphthalene (3.28 g, 10.9 mmol) was added to a solution of
25 mL acetone and 25 mL water. The reaction mixture was stirred at
reflux for 48 hours. After 17 hours, 25 mL more acetone was added.
The reaction mixture was diluted with ether (200 mL) and the organic
phase washed twice with water, once with 10% NaHCO₃, and once with
brine. After drying over MgSO₄, the solvent was removed in vacuo
to afford 2.56 g (99% yield) crude product which could be further
purified by thin layer chromatography (silica gel, CH₂Cl₂), mp 101-
103°C. ¹H NMR (CDCl₃) δ 2.30 (br s, 1H), 4.92 (br s, 2H), 7.25-
7.85 (m, 5H), 8.10-8.35 (m, 1H).

1-Bromo-2-(p-toluenesulfenatomethyl)naphthalene. p-Toluene-
sulfinyl chloride (0.258 g, 1.48 mmol) was added to a chilled solution
of 1-bromo-2-(hydroxymethyl)naphthalene (12) (0.346 g, 1.46 mmol)
and pyridine (0.117 g, 1.48 mmol) in 5 mL anhydrous ether. A white
precipitate appeared immediately. The reaction mixture was then
allowed to stir at ice bath temperature for 2.5 hours, diluted with
40 mL of ether and filtered. The filtrate was washed with dilute (1N)
HCl, water, and 5% NaHCO₃. After drying over MgSO₄, the solvent
was removed in vacuo to yield 0.421 g (76% yield) of a white solid
mp 91-93°C. NMR (CDCl₃) δ 2.30 (s, 3H), 4.90 and 5.30 (AB q, J=12 Hz
and 2 Hz), 7.15-7.80 (m, 9H), and 8.10-8.30 (m, 1H).

1-Bromo-2-(p-toluenesulfonatomethyl)naphthalene (13). A solution
of m-chloroperbenzoic acid (0.066 g, 0.38 mmol) in 1.4 mL dichloro-
methane was added dropwise to a chilled (ice bath) solution of the
sulfinate prepared above (0.100 g, 0.266 mmol) in 1.9 mL of dichloromethane. After stirring for three hours, another 0.38 mmol of m-chloroperbenzoic acid was added and the resulting solution stirred an additional 4 hours while maintaining ice bath temperature for the entire period. The reaction mixture was diluted with dichloromethane and filtered. The filtrate was washed three times with cold 5% NaHCO₃ and twice with cold water. After drying over MgSO₄, the solvent was removed in vacuo at 0°C to yield 0.049 g (47% yield) of a white solid which could be further purified by TLC (silica gel, CH₂Cl₂) at 0°C, mp 77-78°C. NMR (CDCl₃) δ 2.35 (s, 3H), 5.35 (s, 2H), 7.15-7.90 (m, 9H), 8.10-8.30 (m, 1H). The exact mass was 389.9919 (calcd for C₁₈H₁₅BrO₃S: 389.9925).

Naphtho[a]cyclopene (2). n-BuLi (1.13 mL of 2.4 M, 2.71 mmol) was added dropwise to a solution of tosylate 13 (0.89 g, 2.37 mmol) in 27 mL dry THF at -78°C. The reaction was stirred vigorously at this temperature for 15 minutes, then placed in a freezer at -15°C for 10.5 hours with no agitation. The color changed from dark green to yellow during this period. The reaction mixture was then poured into ice water and extracted with cold petroleum ether. The organic phase was separated, washed three times with ice water and dried over MgSO₄. Concentration in vacuo at -35°C yielded 2 as a foul-smelling white solid. NMR (CDCl₃, -30°C) δ 3.40 (s, 2H), 7.25-8.10 (m, 6H). The yield was estimated from the following experiment as 4%.

1-(tert-Butoxymethyl)naphthalene (14) and 2-(tert-Butoxymethyl)naphthalene (15). The crude 2 from above was dissolved in 10 mL CHCl₃ at -25°C. In rapid succession, 10 mL of tert-butyl alcohol and a
catalytic amount of AgBF$_4$ were added. The reaction mixture was then allowed to warm to 0°C over a period of 1.5 hours and stirred at ice bath temperatures for 2.5 hours. The reaction mixture was poured into ice water and extracted with petroleum ether. The organic phase was washed four times with water and dried over MgSO$_4$. Solvent removal in vacuo yielded 20.6 mg crude product (4.0% yield from the tosylate) as a 5:3 mixture of $^{14}$ and $^{15}$ respectively.
References


Reactions of a
Substituted Methylene cyclopropene

I. Background

The "microcyclic" compound methylene cyclopropene (I) has generated a great deal of synthetic and theoretical interest among chemists. The reasons for this are twofold: 1) the large amount of strain involved in having three sp\textsuperscript{2}-hybridized carbons in a three-membered ring and 2) the stabilization gained via the charge-separated resonance structure 1a.

\[
\begin{align*}
\text{I} & \rightleftharpoons \text{1a} \\
\end{align*}
\]

Chemists have created semi-stable substituted analogs by placing substituents at positions which stabilize resonance form 1a. Structures 2 through 5 illustrate this approach.\textsuperscript{1,2} These
structures all have strongly electron-withdrawing groups at the 4-position to stabilize the negative end of the dipole of structure \( \sim \). The negative charge at the 4-position can also be stabilized by incorporating it in a cyclopentadienyl system, as illustrated in structure \( \sim \). The alternative approach, that is to stabilize the positive end of the dipole with strongly electron-donating substituents, does not appear to have been investigated.

Methylenecyclopropenes can also be stabilized by placing bulky substituents on the perimeter of the molecule. This approach has been used by Billups and Blakeney\(^3\) to prepare the substituted methylenecyclopropenes \( \sim \) and \( \sim \).

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

Until recently, attempts to isolate relatively unsubstituted methylenecyclopropenes met with little or no success. Hedaya and coworkers\(^4\) for example attempted to prepare the parent unsubstituted methylenecyclopropene via pyrolysis of \( \text{cis-1-methylene-2,3-dicarboxylic anhydride} \)\(^{9}\). While the mechanism of this process may indeed involve
As an intermediate, the evidence does not exclude such initial processes as fission of the C-2 to C-3 bond to form diradical due to heat.

More recently, Stang and coworkers\textsuperscript{5} prepared tetramethylmethylenecyclopropene via addition of a vinyl carbene to a substituted acetylene as shown below.

The only report, to date, of the synthesis of the parent, unsubstituted methylenecyclopropene comes in the work of Billups, Blakeney, and Chamberlain.\textsuperscript{6} Compound \textsuperscript{1} is, in fact, not isolated but inferred as an intermediate in the base-induced elimination of 1,2-dichloro-1-methylcyclopropane (\textsuperscript{11}) and in the elimination of the sulfone \textsuperscript{12}. 

\[ \text{CH}_3\text{CH}_2\text{Cl} \] 
\[ \rightarrow \text{KO-t-Bu} \] 
\[ \text{Cl} \] 
\[ \rightarrow \text{KSCMe}_2 \] 
\[ 1) \text{KSCMe}_2 \] 
\[ 2) \text{H}_2\text{O} \] 
\[ \text{Me} \]
The modes of reaction of methylenecyclopropene are characterized chiefly by simple nucleophilic addition to carbons 2 and 3, and electrophilic addition to carbon 4. The examples below illustrate this. Methylenecyclopropenes are also frequently trapped with dienes, dipolarophiles, and dienophiles.
II. Results and Discussion

This section concerns the reactions of the 2-substituted methylenecyclopropenes $\sim_{13}$ (X=Cl, O-t-Bu, SMe). In each case studied, the 2-substituent is able to provide electron density to the cyclopropene ring via donation of electron pairs as in structure $\sim_{13a}$.

$\sim_{13}$

$\sim_{13a}$

These reactions were discovered, rather accidentally, while investigating the chemistry of 2,2-dichloro-1-methylenecyclopropene ($\sim_{14}$). Compound $\sim_{14}$ had been previously prepared by Dolbier, Garza, Harmon, and Tarrant$^8$ as a 50:50 mixture of $\sim_{14}$ and ethyl-methyl carbonate. The reaction involves addition of dichlorocarbene, generated from reaction of ethyl trichloroacetate with base, to allene.

\[
\text{CCl}_3\text{CO}_2\text{Et} \xrightarrow{\text{MeO}^-} :\text{CCl}_2 + \text{MeOCO}_2\text{Et} + \text{Cl}^-
\]

$:\text{CCl}_2 + \xrightarrow{\text{MeO}^-} \sim_{14}$

As further purification of $\sim_{14}$ was not required for their work, they made no attempt to isolate pure material.

We found that separation of $\sim_{14}$ from ethyl methyl carbonate impossible by either distillation or column chromatography and thus modified the procedure by using sodium n-butoxide or sodium n-propoxide
as base. In this fashion \[14\] could be isolated in pure form (19% yield) by simple distillation with the by-product, butyl-methyl carbonate, distilling considerably higher.

Reaction of \[\sim\] with potassium \textit{tert}-butoxide in THF yields a mixture of \textit{trans} and \textit{cis}-\textit{tert}-butoxybut-1-ene-3-yne in a ratio of 83:14 respectively with 42% overall recovery. A non-isolable substance \(\sim\) is also produced in the reaction. All attempts to purify \(\sim\) failed, but it is thought to be 2,2-di-\textit{tert}-butoxy-1-methylene-cyclopropene by \(\textbf{\textit{H}}\) NMR of the crude product.

The origin of the vinylacetylenes \(\sim\) and \(\sim\) at first appears puzzling. A mechanism which would account for these products appears on the next page. Addition of \textit{tert}-butoxide to the initially produced chloromethylene-cyclopropene \(\sim\) yields carbene \(\sim\) which rearranges to cumulene \(\sim\) and is finally isomerized to the vinylacetylene. Rearrangement of cyclopropyl carbenes to allenes is a well-documented
procedure as is the addition of nucleophiles to carbons 2 and 3 of methylenecyclopropenes.

In order to further clarify the mechanism of this unusual reaction, the elimination was performed in the presence of the strong nucleophile KSMe. The overall recovery of material was much higher (91%) in this case with the products being a 56:44 mixture of the 2,2-disubstituted methylenecyclopropenes 21 and 22 respectively.

The mechanistic rationale for these products was even more difficult. It was thought at first that these products might simply be due to substitution at the 2-carbon of the methylenecyclopropene. Of course, Sn2 substitution reactions of cyclopropenes are virtually unknown, but this might be a special case of dissociation of one of
the geminal chlorides to form the allylic carbonium ion 23 which would then capture a nucleophile. It is worthwhile to note that this would also entail an extremely strained cyclopropane with two of the carbons sp²-hybridized.

![Diagram](image)

This theory was easily disproven by reacting the starting dichloride with methyl mercaptide in the absence of the base potassium tert-butoxide. The result was that, although the starting dichloride was not recovered, 22 was not among the highly unstable materials recovered.

![Diagram](image)

In light of these experiments, the most likely mechanism to account for products 21 and 22 is shown below. The reason the second

![Diagram](image)
nucleophile chooses to add to the same carbon as the first might be the stability gained by putting a positive charge adjacent to the electron-donating substituent as in resonance structure 23. An analogy to electrophilic substitution mechanisms on aromatic systems is obvious. In these cases also, the most stable resonance structure places positive charge on the electron-donating substituent and assures each atom of a complete octet of electrons. All attempts

\[
\begin{array}{c}
\text{X}^+ \\
\text{E H}
\end{array}
\]

to trap the intermediate substituted methylenecyclopropanes with dienes failed. Apparently, the nucleophilic addition reaction is much faster than the Diels-Alder under these conditions.
III. Experimental

2,2-Dichloro-1-methylenecyclopropane (14). Compound 14 was synthesized by an improved form of the procedure of Dolbier and co-workers. The following procedure allows facile isolation of the desired product with no contamination from dimethylcarbonate.

Sodium n-butoxide was first prepared by the usual method. Thus, dry n-butanol (600 mL, 6.55 mol) was added dropwise to sodium metal (46 g, 2.0 mol) in a one liter three-necked flask equipped with reflux condenser and N₂ inlet over the course of 25 minutes. No external cooling (besides the reflux condenser) is required. The excess butanol is then evaporated by heating to 90°C in vacuo for 10 to 12 hours. Care must be taken that all the butanol is removed before proceeding with the reaction. If sodium n-butoxide is exposed to air, it rapidly decolorizes.

Compound 14 was then prepared as follows. Allene (10 g, 0.25 mol) was added to a slurry of sodium n-butoxide (8.9 g, 90 mmol) and pentane (50 mL) at -75°C. The solution was warmed to -60°C and ethyl trichloroacetate (12 g, 60 mmol) was added in one portion. The reaction was allowed to warm over the course of one hour. At -30°C, the reaction became vigorous and external cooling was required. The reaction was allowed to warm to room temperature overnight. It was then poured into excess water, extracted three times with pentane and the combined organics washed with water four times. After drying over MgSO₄ and concentration in vacuo, the crude product was distilled at atmospheric pressure. Compound 14, bp 95-105°C, was isolated in 19% yield as a clear, colorless liquid.
cis and trans-1-tert-Butoxybut-1-ene-3-yne (16) and (15). 2,2-Dichloro-1-methylenecyclopropane (14) (3.0 g, 24.4 mmol) was added to a solution of potassium tert-butoxide (27.2 g, 24.2 mmol) in 120 mL THF at 0°C. The reaction was allowed to warm to room temperature with stirring over the course of 1.5 hour. Then the reaction was poured into excess water and the solution extracted three times with ether. Then the combined organics were washed six times with water, dried (Na₂SO₄), and concentrated in vacuo to yield 1.27 g (42% yield) of an 83:14 mixture of trans and cis-1-tert-butoxybut-1-ene-3-yne respectively.

2-tert-Butoxy-2-thiomethyl-1-methylenecyclopropane (21) and 2,2-bis(Thiomethyl)-1-methylenecyclopropane (22). Methyl mercaptan (4.70 g, 97.6 mmol) was added to a solution of potassium tert-butoxide (27.2 g, 243 mmol) in 120 mL dry THF while cooling with an ice/salt bath. Then 2,2-dichloro-1-methylenecyclopropane (3.0 g, 24.3 mmol) was added dropwise with ice cooling. The reaction was allowed to warm to room temperature over three to four hours. Then the reaction was poured into excess water and extracted with ether three times. The combined organics were washed with water six times, dried (Na₂SO₄), and concentrated in vacuo to yield 3.54 g (91% yield) of a 56:44 mixture of 21 and 22 respectively. Although 21 could be purified by preparative gas chromatography, 22 did not survive gas chromatography and was purified by preparative TLC (silica gel, CS₂ and CH₂Cl₂, 50:50).

7-Methylenebicyclo[4.1.0]hept-3-ene. 7-Chloro-7-methylbicyclo[4.1.0]hept-3-ene (1.5 g, 10.5 mmol) was added dropwise to a slurry of potassium tert-butoxide (5.90 g, 52.6 mmol) at room temperature.
The reaction was allowed to stir for two hours. The solution was then added to excess water and the product extracted three times with pentane. The combined organics were then washed three times with water, dried (Na₂SO₄), and concentrated in vacuo to yield 0.84 g (75% yield) of a 53:29:18 mixture of 7-methylenebicyclo[4.1.0]hept-2-ene, 7-methylenebicyclo[4.1.0]hept-3-ene, and ethylbenzene respectively.
References


LOCK POS. 100 ppm
LOCK POWER 1.0 W
DECOUPLE POS. 100 ppm
DECOUPLING POWER 1.0 W
SPECTRUM AMPL. 100
Sweep Time 1 min
Nucleus 1 H
Sample
Filter 0.55 N
Sweep Width 12 ppm
Zero Ref. 12 ppm
End of Sweep 15 ppm
Sample Temp. Ambient
Solvent: CCl₄
LOCK POS. 0.0  ppm  SPECTRUM AMPL. 0.0  SWEEP TIME 5  min  NUCLEUS 1H  SAMPLE:
LOCK POWER 0.0  mG  FILTER 0.0  Mc  SWEEP WIDTH 10  ppm  ZERO REF. 10  Mc  
DECOUPLING POS. 0.0  ppm  RF POWER 0.0  mG  END OF SWEEP 0.0  ppm  SAMPLE TEMP. 0°C  SOLVENT: 

\[ \Delta \sin \theta \]
Appendix:
The Reaction of Collman's Reagent
with Carbon Dioxide

Collman's reagent$^1$ [disodium tetracarbonylferrate-dioxane (2:3)]
(1) is known to react with a variety of alkyl and acyl halides. The
alkyliron compounds formed can then be treated with acetic acid to
yield aldehydes or with a second equivalent of an alkyl halide to
yield ketones.$^2$ In view of the recent interest in finding organo-
metallic compounds which bind CO$_2$, we thought it logical to attempt
to make a CO$_2$ adduct of Collman's reagent.

\[
\begin{align*}
\text{Na}_2\text{Fe(CO)}_4 & \rightarrow \text{OC} \\
& \quad \text{Fe} \\
& \quad \text{CO} \\
& \quad \text{CO} \\
& \quad \text{R} \\
& \quad \text{HOAc} \rightarrow \text{RCHO} \\
& \quad \text{R}^+\text{X} \rightarrow \text{RCR}
\end{align*}
\]

As Collman's reagent is known to be extremely nucleophilic in
solutions of DMF and N-methylpyrrolicinone, DMF was chosen as the
reaction solvent. We found that simple treatment of a slurry of
Collman's reagent in DMF with carbon dioxide (at 1.1 atm pressure)
resulted in the uptake of approximately one equivalent of CO$_2$ over
the course of two days. An orange solid could be isolated from the
reaction medium. IR and $^1$H NMR indicate that this solid has one
coordinated DMF. An IR absorption at 1670 cm$^{-1}$ was initially atributed
to a coordinated CO$_2$, now seems to belong to the coordinated DMF.
However, the possibility that this is obscuring another absorption
has not been investigated. Further IR absorptions are at 1920 cm\(^{-1}\) and at 1860 cm\(^{-1}\). The two carbonyl absorptions are consistent with terminal (non-bridging) carbonyls or with the carbonyls of metal anions. The powdery nature of this material (extremely difficult to crystallize) seems to indicate that it is indeed a salt.
Experimental

Reaction of Disodium Tetracarbonylferrate (Collman's Reagent) with Carbon Dioxide in DMF. A slurry of Na₂Fe(CO)₄·1.5(C₄H₈O₂) (2.0 g, 5.78 mmol) in DMF (freeze-thaw degassed) was allowed to stir under CO₂ (anaerobic) for approximately two days. During this period, approximately one equivalent CO₂ was absorbed. The solution was then transferred to a glove box and poured into 500 mL Et₂O (degassed). An orange solid precipitated which was washed several times with ether. It was soluble in THF, DMF, acetone, and other polar solvents and had a mp=100-102°C (dec). It was insoluble in ether and hexanes. The solid could be dissolved in THF and reprecipitated with ether resulting in an overall increase in quality. At no point, however, could x-ray quality crystals be grown. After several days in the glove box, the material became reddish. Redissolving in THF followed by precipitation with ether resulted in orange material again. The ¹H NMR (d₆-acetone) revealed a coordinated DMF. It was impossible to achieve suitable concentrations for ¹³C NMR.
References


INDEX OF SPECTRA

3,4-Benz-1-bromo-6,6-dichlorobicyclo[3.1.0]hexane, 38, 39.
3,4-Benz-1,6-dichlorobicyclo[3.1.0]hexane, 71, 72.
3,4-Benz-1,6,6-trichlorobicyclo[3.1.0]hexane, 67, 68.
1,3-Bis(N,N-dimethylamino)naphthalene, 63, 64.
1-Bromo-2-chloronaphthalene, 42, 43.
1-Bromo-2-(hydroxymethyl)naphthalene, 83, 84.
1-Bromo-2-(p-toluenesulfinatomethyl)naphthalene, 85, 86.
1-Bromo-2-(p-toluenesulfonatomethyl)naphthalene, 87, 88.
cis-1-tert-Butoxybut-1-ene-3-yne, 104, 105.
trans-1-tert-Butoxybut-1-ene-3-yne, 106, 107.
1-tert-Butoxy-2-chloronaphthalene, 48, 49.
2-tert-Butoxy-3-chloronaphthalene, 50, 51.
1-(tert-Butoxymethyl)naphthalene and 2-(tert-Butoxymethyl)naphthalene, 89.
2-tert-Butoxy-2-thiomethyl-1-methylene cyclopropane, 110, 111.
2-Chloro-1-(N,N-dimethylamino)naphthalene, 59, 60.
2-Chloro-3-(N,N-dimethylamino)naphthalene, 61, 62.
2-Chloroindene, 65, 66.
2-Chloronaphthalene, 40, 41.
2-Chloronaphthalene ($^{13}$C NMR), 57.
2-Chloro-1,3-dideuteronaphthalene ($^{13}$C NMR), 58.
2-Chloro-3-phenyl naphthalene, 69, 70.
2-Chloro-1-(2'-tetrahydrofurfuryl)naphthalene and 2-Chloro-3-(2'-
tetrahydrofurfuryl)naphthalene, 55, 56.
1,3-Di(tert-butoxy)naphthalene, 52, 53, 54.
2,2-Dichloro-1-methylenecyclopropene, 103.
1,2-Dichloronaphthalene, 44, 45.
2,3-Dichloronaphthalene, 46, 47.
7-Methylenebicyclo[4.1.0]hept-3-ene, 112, 113.
Naphtho[a]cyclopropene, 89.