INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. 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 original submitted.

The following explanation of techniques is provided to help you understand markings or patterns 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 thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

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

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs” if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
FRIEDLI, Floyd E.
THE CHEMISTRY OF 1H-CYCLOBUTA[de]NAPHTHALENES.
The Ohio State University, Ph.D., 1978
THE CHEMISTRY OF 1H-CYCLOBUTA[de]NAPHTHALENES

DISSERTATION
Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By
Floyd E. Friedli, B.A.

The Ohio State University
1978

Reading Committee:

Dr. Melvin S. Newman
Dr. Carter Olson
Dr. John A. Secrist III
Dr. H. Shechter

Approved by

Adviser
Department of Chemistry
ACKNOWLEDGMENTS

I would like to thank Professor Harold Shechter for his suggestion of the research problem and his multitude of ideas which were used in developing it to the fullest. I thank Dr. Peter Card for expanding my chemical knowledge both mentally and experimentally. These two men helped make me the chemist I am.

David Green's synthetic help is also greatly appreciated.

Most of all, I thank my wife, Patti, and my parents for loving me despite the trials and tribulations of being a graduate student.
VITA

February 2, 1951. . . . . . Born, Coshocton, Ohio

1973 . . . . . . . . . . . . B.A., College of Wooster
    Wooster, Ohio

1973 - 1974 . . . . . . . Graduate Student, The Ohio
    State University, Columbus
    Ohio 43210

1975 - 1978 . . . . . . . Research Associate, The
    Ohio State University,
    Columbus, Ohio 43210

Field of Study: Organic Chemistry
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td><strong>PART I</strong></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>2</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>11</td>
</tr>
<tr>
<td>Synthesis of 1H-Cyclobuta[de]naphthalene</td>
<td>11</td>
</tr>
<tr>
<td>Electrophilic Substitution</td>
<td>14</td>
</tr>
<tr>
<td>Chemistry of Electrophilic Products</td>
<td>26</td>
</tr>
<tr>
<td>Free Radical and Carbonium Ion Chemistry</td>
<td>32</td>
</tr>
<tr>
<td>Chemistry at the Bridging Carbon</td>
<td>50</td>
</tr>
<tr>
<td>Spectral Properties of 1H-Cyclobuta[de]-naphthalenes</td>
<td>73</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>88</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>161</td>
</tr>
<tr>
<td><strong>PART II</strong></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>165</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>166</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>170</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>175</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>181</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Comparative Rates of Electrophilic Substitution of 49, 50, 52, and 1</td>
<td>23</td>
</tr>
<tr>
<td>2.</td>
<td>Position of Deuterium Label upon Quenching 4-Lithio-1H-cyclobuta[de]napththalene (58) at Various Time Intervals with D2O</td>
<td>31</td>
</tr>
<tr>
<td>3.</td>
<td>Products of Hydrogen Bromide Addition to Olefins 22, 23, 24, and 25</td>
<td>34</td>
</tr>
<tr>
<td>4.</td>
<td>Relative Rate of Deuterium Exchange on 9-Cyanofluorene (110), Diphenylacetonitrile (111) and 1-Cyclobuta[de]napththalene (108)</td>
<td>64</td>
</tr>
<tr>
<td>5.</td>
<td>Chemical Shifts (δ) of the Methyl and Methylene Protons of Substituted Toluenes, Diphenylmethanes, and 1H-cyclobuta[de]-napththalenes</td>
<td>77</td>
</tr>
<tr>
<td>6.</td>
<td>C13 NMR Data (δ) of 1H-Cyclochbuta[de]napththalenes</td>
<td>80</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The Bond Lengths (Å) of 1H-cyclobuta[de]-naphthalene (1) and Naphthalene (52).</td>
<td>20</td>
</tr>
<tr>
<td>2.</td>
<td>The Bond Angles (°) of 1H-cyclobuta[de]-naphthalene (1) and Naphthalene (52).</td>
<td>20</td>
</tr>
<tr>
<td>3.</td>
<td>The Important Bond Angles (°) of Acenaphthene (49) and 1,8-Dimethylnaphthalene (51).</td>
<td>20</td>
</tr>
<tr>
<td>4.</td>
<td>Partial NMR of 1H-Cyclobuta[de]naphthalene (1).</td>
<td>74</td>
</tr>
<tr>
<td>5.</td>
<td>Aromatic Splitting Pattern of 4-Nitro-1H-cyclobuta[de]naphthalene (42).</td>
<td>75</td>
</tr>
<tr>
<td>6.</td>
<td>The C¹³ NMR of 1-Chloro-1H-cyclobuta[de]-naphthalene (112).</td>
<td>78</td>
</tr>
<tr>
<td>7.</td>
<td>Partial Proton NMR of Tetrabromide 75.</td>
<td>82</td>
</tr>
<tr>
<td>8.</td>
<td>Partial Proton NMR of Pentabromide 81b.</td>
<td>84</td>
</tr>
<tr>
<td>9.</td>
<td>Partial NMR of Pentabromide 81a.</td>
<td>85</td>
</tr>
</tbody>
</table>
PART I

INTRODUCTION

The present research involves investigation of 1H-cyclobuta[de]naphthalene (1) and analogs of this peri-single atom bridged system. The inherent stability of 1, its reactions with various reagents particularly electrophiles, and the synthesis of numerous derivatives of this unique molecule are the objectives of this study.
Organic chemists have always been fascinated with the unusual; be it structure or reactivity. Single-atomed peri-bridged naphthalenes are thus ideal for study because they exhibit both of these characteristics. Besides developing new synthetic methodology, such investigations provide valuable information on bonding, stability, and new reactions of highly strained molecules. This information expands the scope and theory of organic chemistry.

Single-atomed peri-bridged naphthalenes have only recently been available for study.

Sulfur compounds naphtho[1,8-bc]thiete 1,1-dioxide (2) and naphtho[1,8-bc]thiete (3) were prepared by photolysis of heterocycles naphtho[1,8-de]1,2,3-thiadiazine 1,1-dioxide (6), and naphtho[1,8-cd]1,2 dithiole 1,1-dioxide (7) (Equations 1 and 2).^1,2
1-Bromo-1H-cyclobuta[de]naphthalene (4) was first synthesized in 40% yield in this laboratory by photolysis of 8-bromo-1-naphthylidiazomethane (8) in diethyl ether (Equation 3).

Formation of 4 presumably occurs by loss of nitrogen to give 8-bromo-1-naphthylidene, then probably by coordination
of the carbene with the peri-bromine to form an ylid that rearranges to 4.

Silicon in the bridging position as 5 was introduced by reaction of 1,8-dilithionaphthalene (9) with dialkyl-dichlorosilanes (Equation 4). 4

\[
\text{Li Li} + \text{R}_2\text{SiCl}_2 \rightarrow \text{Si} \quad \text{(4)}
\]

1,8-Dimetallonaphthalenes (9, 10) have also proven useful for an alternate preparation of 1H-cyclobuta[de]naphthalene (1) in respective yields of 9% and 19% (Equation 5). 5

\[
\text{M M} + \text{H}_2\text{CX}_2 \rightarrow \text{H} \quad \text{(5)}
\]

9, M = Li; 11, X = Cl
10, M = Mg-I; 12, X = OTs

The stabilities of the various single atom bridged naphthalenes vary greatly. Bridged sulfide 3 is very reactive to nucleophiles (Equation 6). 1
Silicon analogs $\text{5}$ are moisture sensitive (Equation 7).

The 1H-cyclobuta[de]naphthalene system is by far the most interesting of the single atom peri-bridged naphthalenes. Bromide $\text{4}$ reacts with a wide variety of nucleophiles to give displacement products (Equation 8) without ring opening.

However, displacements involving hydroxide ion and amines result in highly unstable intermediates (such as alcohol $\text{17}$ in Equation 9) which isomerize to more stable products.
It is apparent that the lone pair electrons of the substituents introduced play important roles in the ring opening reactions. Acetate $^{18}$ and tosylate $^{19}$ are quite stable, however, at room temperature (Equation 10).

As yet the most useful nucleophilic displacement of $^{4}$ occurs with triphenylphosphine (Equation 11) in refluxing xylene. Ylid $^{21}$ formed from phosphonium salt $^{20}$ and $t$-butyllithium reacts efficiently (80-85%) with aldehydes and ketones (Equation 11) to give $^{22}$ - $^{25}$.
These highly strained olefins are surprisingly stable, but undergo specific thermal diradical rearrangements as illustrated for 23 (Equation 12).

Further, ozonolysis of 24 provides a route to 1H-cyclobuta[de]naphthalene-1-one (26, Equation 13).

Ketone 26 is fairly stable, but undergoes ring opening with nucleophiles such as water (acid or base-catalyzed, as in Equation 14), alcohols, amines, and hydrazine derivatives.

\[ \text{23} \xrightarrow{600^\circ} \text{23} \]

\[ \text{24} \xrightarrow{1) O_3, 2) DMS} \text{26} \]

\[ \text{26} \xrightarrow{H_2O} \text{27} \]
Some progress has been made in the generation and use of the carbonium ion $28$, free radical $29$, and carbanion $30$ at the C-1 bridging position. Tosylate $19$ solvolyzes (Equation 15) much slower in acetic acid than do 9-fluorenyl tosylate and benzhydryl tosylate. This may indicate that internal strain present in the $1H$-cyclobuta-$[de]$naphthalene system is hindering formation of the carbonium ion.

\[
19 \xrightarrow{-\mathrm{OTs}} 28 \quad \text{HOAc} \rightarrow 18 \quad (15)
\]

The $1H$-cyclobuta-$[de]$naphthalen-1-yl radical ($29$) is the presumed intermediate generated in the bromination of hydrocarbon $1$ with $N$-bromosuccinimide and a free radical initiator (Equation 16).

\[
1 \xrightarrow{\text{Init.}} -\mathrm{H} \rightarrow 29 \xrightarrow{\text{NBS}} 2 \quad (16)
\]
Deuterium exchange studies on hydrocarbon 1 using sodium dimethylsulfoxide/DMSO-d₆ show the acidity of the peri-bridge hydrogens (Equation 17).

\[
\begin{align*}
\text{Na}^+ & \quad \text{DMSO-d₆} \\
\text{1} & \quad \text{D₂C-S-CD₃} \\
\end{align*}
\]

\[(17)\]

The conversion of bromide 2 into the corresponding organometallics 30 and 31 and their capture with electrophiles illustrates the synthetic utility of the carbanion at the bridge carbon (Equation 18).

\[
\begin{align*}
\text{2} & \quad \text{Mg or BuLi} \\
\text{M} & \quad \text{H} \\
\text{RX} & \quad \text{M} \quad \text{H} \\
\end{align*}
\]

\[(18)\]

\[
\begin{align*}
30, \quad M & = \text{MgBr} \\
31, \quad M & = \text{Li} \\
32, \quad R & = \text{CH₃} \\
33, \quad R & = \text{C-CH₃} \\
\end{align*}
\]

Ring cleavage of 1 does occur to give 1-methylnaphthalene (100%) upon catalytic hydrogenation (2 atm) over palladium/carbon (Equation 19).

\[
\begin{align*}
\text{1} & \quad \text{H₂} \quad \text{Pd/C} \\
\text{CH₃} & \quad \text{Pd/C} \\
\end{align*}
\]

\[(19)\]
Only a brief summary is presented here of the work done on the 1H-cyclobuta[de]naphthalene system by Card and Bailey; their theses give a more elaborate description of the chemistry that has been explored.
RESULTS AND DISCUSSION

Synthesis of 1H-Cyclobuta[de]naphthalene

This research involves a broad range exploration of the chemistry of the 1H-cyclobuta[de]naphthalene system. Studies planned for hydrocarbon 1 and bromide 4 include:

1) electrophilic substitution; 2) comparative rates of electrophilic substitution; 3) generation, stability, and use of reactive intermediates at the bridging carbon; and 4) synthesis and chemistry of a number of derivatives of 1H-cyclobuta[de]naphthalene. This open-ended investigation thus requires a sizable quantity (100-150 g) of bridged naphthalenes 1 and 4 and their derivatives.

Since synthesis of 4 is non-trivial requiring eight steps in an overall yield of 7-9%, it is necessary that the preparation be as efficient as possible. A major initial effort in this research was directed toward simplifying the chemistry and the experimental procedures used. 1H-Cyclobuta[de]naphthalene (1) has now been prepared by modification of the methods by Bailey and Card. Though yields have only been minimally improved, the synthesis is quicker, cheaper, and less cumbersome.
Greater quantities of 1 and 4 can be accumulated with less effort. The overall synthesis of 4 is illustrated in Scheme 1 and Equation 3.

Hydrolysis of 1,8-naphthalic anhydride (34) followed by reaction with mercuric acetate and thermal decarboxylation gives a 97% yield of anhydro-8-hydroxymercuri-1-naphthoic acid (35). Bromination of 35 produces 8-bromo-1-naphthoic acid (36, 64%), which is easily converted to 8-bromo-1-naphthoyl chloride (37, 86%) by thionyl chloride. Reduction of acid chloride 37 with lithium aluminum hydride to 8-bromo-1-naphthalenemethanol (38, 88%) and subsequent oxidation by N-chlorosuccinimide and dimethyl sulfide yields the key intermediate 8-bromo-1-naphthaldehyde (39, 85%). Aldehyde 39 reacts readily with p-tosylhydrazide to give 8-bromo-1-naphthaldehyde p-tosylhydrazone (40, 80%, Scheme 1).

Alternatives that were attempted and developed include Rosenmund reduction of acid chloride 37 which gives both 8-bromo-1-naphthaldehyde (39, 23%) and 1-naphthaldehyde (41, 34%). Obviously, this result is unacceptable. Phase transfer oxidation using sodium hypochlorite provides another method of preparation of
Scheme 1

\[
\begin{align*}
34 & \xrightarrow{1) \text{NaOH}} \xrightarrow{2) \text{Hg(OAc)}_2} 35 & \xrightarrow{\text{Br}_2} 36 \\
& \xrightarrow{\text{NCS, DMS or NaOCl P.T.}} \xleftarrow{\text{BrCHO}} 39 & \xrightarrow{\text{LAH}} 37 \\
& \xrightarrow{\text{H}_2\text{NNHTs}} \xleftarrow{\text{BrCH=N-NHTs}} 40 \\
\end{align*}
\]
The yield is good (>80%) and the reagents less costly and odoriferous than the original method (Scheme 1).

Tosylhydrazone 40 is treated with sodium hydride and photolyzed in diethyl ether to yield bromide 4 via in situ generation of diazo compound 8 (Equation 3). 1H-Cyclobuta-[de]naphthalene (1) is prepared quantitatively from 4 using sodium bis(2-methoxyethoxy)aluminum hydride.

Experimentally, it is noted that 37, 38, and 39 can be used in crude form without recrystallization. This saves time and improves the yields. Recrystallization of 40 and the necessary chromatography to isolate 4 removes all undesirable materials.

**Electrophilic Substitution**

The question of how electrophiles react with hydrocarbon 1 is important. Two courses of attack are probable: 1) rupture of the bridge giving a benzylic carbonium ion or 2) aromatic electrophilic substitution (Equation 19).

\[
1 \quad \xrightarrow{E^+} \quad \begin{array}{c} \text{E} \\ \text{CH}_2 \end{array} \quad + \quad H^+ \quad (19)
\]
Aromatic substitution has the added aspect of orientation preferences.

Nitration of 1 using nitric acid, sulfuric acid, and acetic acid or the milder acetyl nitrate produces 4-nitro-1H-cyclobuta[de]naphthalene (42) and smaller amounts of 4,5-dinitro-1H-cyclobuta[de]naphthalene (43, Equation 20).

\[ \overset{\text{NO}_2}{1} \rightarrow \overset{\oplus}{\text{NO}} \text{NO}_2 \]

Breaking of the cyclobutyl ring does not occur and orientation other than para* substitution is not seen. Yields up to 85% can be obtained for 42. The structure of 42 is established by its combustion analysis and spectral properties including exact mass. The aromatic region off the nmr reveals a 12 line spectrum consistent with its assignment as a 4-substituted isomer. (See Spectra chapter for a summary and explanation of data for new compounds). The methylene absorbs at 6 4.73 and the infrared contains peaks at 1505 and 1300 cm\(^{-1}\) for the nitro group.
Dinitro compound 43, which is also preparable by separate nitration of 42 using nitric acid and sulfuric acid, exhibits 2 nmr doublets in the aromatic region (δ 7.39 for the ortho and 8.85 for the meta). Nitro absorptions at 1510 and 1315 cm⁻¹ in the infrared, combustion analysis, exact mass, and a 7 line C¹³ nmr confirm the symmetrical structure of 43.

Nitration of bromide 4 with acetyl nitrate gives only 1-bromo-4-nitro-1H-cyclobuta[de]naphthalene (44). Its structure is assigned using combustion analysis, exact mass, and spectral properties. Again, the nmr of the aromatic region exhibits 12 lines indicating para substitution. Nitro compound 44 is the first derivative of 1 with a chiral bridge carbon.

Acetylation of hydrocarbon 1 using acetyl chloride and aluminum chloride in dichloromethane yields 4-acetyl-1H-cyclobuta[de]naphthalene (45, 61%, Equation 21). No other products (orientation or ring breakage) are seen. The structure is based on the spectral properties, exact mass, and combustion analysis of ketone 45 and the exact mass and elemental analysis of its 2,4-dinitrophenylhydrazone. The aromatic region of the nmr of 45 shows a
characteristic 12 line spectra of a 4-substituted isomer; the methylene absorbs at δ 4.53 and the methyl at 2.51. An infrared carbonyl absorption occurs at 1665 cm⁻¹.

Friedel-Crafts reaction of 1 with phenylacetyl chloride in the presence of aluminum chloride also results only in para-substitution. Spectra, exact mass, and combustion analysis confirm the product as 4-(1-phenyl-acetyl)-1H-cyclobuta[de]naphthalene (46, Equation 21). The isolated yield (87%) is considerably higher than for the previous case, though the reason is unknown.

Attempts to di-acylate 1 in refluxing 1,2-dichloroethane fail.

Electrophilic bromination of 1 proceeds easily to give 4-bromo-1H-cyclobuta[de]naphthalene (47, 94%, Equation 22). Supportive evidence for the structure of 47 comes from its exact mass and spectral properties, and the combustion analysis of the bromide (47) and its picrate.
The nmr of 47 being non-descript prohibits a definite assignment of para substitution. Independent synthesis of 47 (see Chemistry of Electrophilic Products chapter) was thus necessary.

4,5-Dibromo-1H-cyclobuta[de]naphthalene (48), prepared by bromination of 47 in 89% yield, is of proper mass and analysis and exhibits the characteristic spectrum of a symmetrical peri-bridged naphthalene. The C\textsuperscript{13} nmr shows 7 lines and the proton nmr 2 doublets in the aromatic region at δ 6.82 and 7.59.

The 1H-cyclobuta[de]naphthalene system does not ring open upon reaction with a variety of electrophilic reagents - nitric acid, aluminum chloride, bromine, etc. As yet the only electrophilic ring opening of 1 is by silver ion (acetate) giving 1-naphthalenemethanol acetate.\textsuperscript{6} Aromatic electrophilic substitution of hydrocarbon 1 under a variety of conditions occurs regiospecifically at the 4-position. This contrasts sharply with the known electrophilic reactions of acenaphthlene (49), 2,3-dihydrophenalene (50), and 1,8-dimethylnaphtalene (51). Even under the
mildest, most selective of conditions bromination of hydrocarbons 49, 50, and 51 result in 3-8% ortho mono-bromides the remainder being para. Similar percentages are obtained for nitration of acenaphthene (49). Naphthalene, of course, substitutes in the \( \alpha \)- and in the \( \beta \)-positions.

The x-ray structure of 1 gives insight into the clean electrophilic reactions of the 1H-cyclobuta[de]-naphthalene system. Figures 1 and 2 compare the bond lengths and angles of 1 and naphthalene (52). Figure 3 gives the important angles of 49 and 51. The strain in the cyclobutane ring in 1 and 4 is partly dissipated throughout the naphthalene moiety and this explains the surprising stabilities of these bridged arenes. Bridging the peri positions of naphthalene with a single-carbon moiety severely compresses the portion of the naphthalene nucleus directly connected to the bridge and expands the opposite side of the molecule. The shortened aromatic bonds near the bridge should be correspondingly stronger, while the elongated bonds would be weaker and more susceptible to attack. Thus, the specific reactions of electrophiles at C-4 of 1 are reasonable.
Figure 1. The Bond Lengths (Å) of 1H-cyclobuta[de]-naphthalene (1) and Naphthalene (52).

Figure 2. The Bond Angles (°) of 1H-cyclobuta[de]-naphthalene (1) and Naphthalene (52).

Figure 3. The Important Bond Angles (°) of Acenaphthene (49) and 1,8-Dimethylnaphthalene (51).
Other comparisons of the 1H-cyclobuta[de]naphthalene system with 49, 50, and 51 show differences in disubstitution patterns. 5-Bromoacenaphthene and 5-iodoacenaphthene brominate, iodinate, and nitrate to give the corresponding 3(ortho)-substituted derivatives as major products (Equation 23).¹¹

\[
\text{Br}_2 + \text{Br} \quad \xrightarrow{\text{Br}_2} \quad \text{Br} + \text{Br} \\
\text{major}
\]

Bromination of 4-bromo-1,8-dimethylnaphthalene yields 2,4-dibromo-1,8-dimethylnaphthalene as the principal product along with 4,5-dibromo-1,8-dimethylnaphthalene.¹¹ These results again contrast with the dibromination of 1, where 4,5-dibromo-1H-cyclobuta[de]naphthalene (48) is the exclusive product (Equation 22). The specificity of electrophilic reactions of 1 caused by its unique structure is dramatic.
A study was undertaken of the comparative rates of electrophilic substitution of 1H-cyclobuta[de]naphthalene (1) versus hydrocarbons 49, 50, and 52. Samples of 1 (10 mmol) were mixed with each of the other hydrocarbons (10 mmol) and these mixtures nitrated, acylated, and brominated under very mild conditions using 1 mmol of the electrophilic reagent. The large excess of reactants insured only a minimal change in the ratio of hydrocarbons as the reaction proceeded. Nitration was accomplished at 0° with acetyl nitrate in acetic anhydride while acetylation was effected with acetyl chloride and aluminum chloride at 25° in dichloromethane. Bromination involved the slow addition of bromine in carbon tetrachloride to a slurry of iron fillings in carbon tetrachloride containing the hydrocarbons in the dark at 0°. The product fraction was then analyzed for a ratio of the substituted arenes (see Experimental section). Each reaction was carried out twice and the results are summarized in Table 1.

A definite trend is observed for the rates of electrophilic substitution - 52 < 1 < 50 < 49. 1H-Cyclobuta[de]naphthalene (1) is faster than naphthalene
TABLE 1
COMPARATIVE RATES OF ELECTROPHILIC SUBSTITUTION
OF 49, 50, 52, AND 1.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Nitration&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Acylation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Bromination&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>49 vs. 52</td>
<td>3.5</td>
<td>8.2</td>
<td>110</td>
</tr>
<tr>
<td>49 vs. 1</td>
<td>8.0</td>
<td>4.2</td>
<td>12.8</td>
</tr>
<tr>
<td>50 vs. 1</td>
<td>4.55</td>
<td>2.6</td>
<td>6.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values determined by nmr analysis.

<sup>b</sup>Values determined by gc analysis.

<sup>c</sup>Values corrected as 52 has twice as many "active" positions as 1.
because of two important structural features. First, 1 is highly strained and more susceptible to attack by electrophiles. Also, 1 possesses the methylene bridge which both by induction and hyperconjugation is an electron-donating group. Acenaphthene (49), in comparison, is less strained than 1, but contains two methylene groups giving it greater electron density in the naphthalene nucleus by induction and hyperconjugation. Possibly for these reasons 49 is significantly more reactive than 1. In the final case, 2,3-dihydrophenalene (50) is relatively unstrained as the angles of the bonds emanating from the peri-positions are 120°. It too possesses high electron density in the aromatic ring and reacts slightly faster than 1.

Table 1 also reveals (through indirect comparison) that acenaphthene (49) substitutes faster than 2,3-dihydrophenalene correlating with the literature.11

A comparison of the transition states involved gives further explanation of the trends observed. The relative rates of reaction may really be due to the relative stabilities of the cationoidal transition states. Five-membered rings (53) can more easily accommodate a
carbonium ion center than a six-membered ring (54) and much more than a four-membered ring (55). This follows the order of $49 > 50 > 1$.

When an electrophile attacks the para position of a strained molecule such as 1 or 49 to give an intermediate like 53 or 55 this causes a significant relief of strain. The para position is temporarily sp$^3$ hybridized with the attached bonds being slightly elongated to carbon-carbon single bond lengths. Thus the portion of the molecule that desires expansion has been expanded.

Table 1, as do all data, may contain errors. It is assumed that the aromatic substitution is non-reversible and the product ratio represents the kinetic ratio. The mild conditions utilized kept the rate of reaction slow and minor products to a minimum ($< 5\%$ for bromination and nitration). Bromination is the slowest and most selective of the reactions studied. With naphthalene (52) acylation is more selective than nitration, but with 49 and 50 acylation is less selective. More significant amounts of ortho products ($10-15\%$) are also clearly
visible for acylation of 49, 50, and 52. These two anomalies indicate the Friedel–Crafts acylation is suspect and may really be reversible to some extent. This violation of the basic assumption best explains the problem data.

Regardless, the trends in Table 1 indicate that both peri-bridging and electron-donating groups enhance the rate of electrophilic substitution. Strain caused by peri-bridging makes a naphthalene derivative more susceptible to attack, while the lack of strain (or higher stability) of carbonium ion intermediates helps the reactions to completion.

Chemistry of Electrophilic Products

It has been previously observed that 1 hydrogenates with ring cleavage to give 1-methylnaphthalene. Aromatic nitro groups are easily reduced to amines by catalytic hydrogenation. A study was commenced of hydrogenation of 42 to see which group, the nitro group or the methano bridge, is affected first and if the reduction could be controlled. It was found that under proper conditions 42 is reduced to 4-amino-1H-cyclobuta[de]-naphthalene (56, Equation 24). No methyl-nitro-naphthalenes
are obtained and longer reaction times, of course, do give amino-methyl-naphthalenes.

\[
\text{42} \quad \text{NO}_2 \quad \stackrel{\text{H}_2 \quad \text{Pd-C}}{\longrightarrow} \quad \text{56} \quad \text{NH}_2
\]  

(24)

Amine 56 is a liquid which rapidly darkens on exposure to air. It exhibits characteristic infrared amine frequencies at 3450 and 3360 cm\(^{-1}\). Additional confirmation of structure comes from other spectral data, the exact mass of 56 and its N-phenyl thiourea derivative, and combustion analysis of the thiourea derivative.

Amine 56 is also obtained from nitro compound 42 using tin and hydrochloric acid as the reducing medium. The yield is low (13%) and a large amount of complex material accompanies the product. Aluminum-amalgam in an ether-ethanol-water mixture produces 56 from 42 in \(~80\%\) yield. This is undoubtedly the method of choice as it gives higher yields and a purer product – the catalytic hydrogenation is tricky to control and the product is usually contaminated with starting material or over-reduced product.
Diazotization of $56$ and heating with cuprous bromide affords $4$-bromo-$1H$-cyclobuta[de]naphthalene ($47$, Equation 25).

\[
\begin{align*}
56 \quad &1) \text{NaNO}_2, \text{HBr} \\
\quad &2) \text{CuBr}, \Delta \\
\end{align*}
\]

This independent synthesis of bromide $47$ through a Sandmeyer sequence gives convincing proof that bromination of $1$ does give $47$ with its bromine in the $4$-position. The yield of the Sandmeyer reaction is low ($11\%$) and much polymeric material is formed.

The disappointing yields in the tin-hydrochloric acid reduction and the Sandmeyer reaction indicate that the $1H$-cyclobuta[de]naphthalene system might not be stable to the strongly acidic reagents. Hydrocarbon $1$ was exposed to tin and hydrochloric acid under the same conditions used for reducing compound $42$. Over $90\%$ of $1$ is recovered. Treating $1$ with refluxing $48\%$ hydrobromic acid produces the same result. Surprisingly, the $1H$-cyclobuta[de]naphthalene system is stable to these conditions - no reduction or cleavage occurs. The low yields from the previous reactions of $56$ are attributed
to the amine moiety and not the ring system. Amine 56 discolors faster than other aromatic amines (for instance 1-naphthylamine) when exposed to the atmosphere and virtually can not be obtained in pure form for further reactions.

Another more far-reaching explanation for the unique properties of this amine is that 56 exists in tautomeric forms (Equation 26).

\[
\begin{align*}
\begin{array}{c}
\text{56} \\
\text{NH}_2
\end{array} & \quad \Longleftrightarrow \quad \\
\begin{array}{c}
\text{57} \\
\text{NH}
\end{array}
\end{align*}
\]

Some aromaticity is lost, but the cyclobutane ring now would contain only 2 sp² carbons and hence would be less strained. This unsaturated imine (57) is expected to be highly reactive.

Interesting studies for the future include synthesis of 4-hydroxy-1H-cyclobuta[de]naphthalene which might have a detectable amount of ketone tautomer. Chemistry of this naphthol including treatment with base and subsequent alkylation could give valuable information on the stabilities of various tautomeric forms.
Bromide $47$ is readily converted to Grignard and lithium reagents which react with acetyl chloride and with acetaldehyde. Both reactions result in useless mixtures containing many components. It seemed apparent that the initially formed organo-metallic reagents are undergoing structural change. A study of deuterium quenching of the products of reaction of $47$ with n-butyllithium reveal conversion of $58$ to $30$. Though only approximate, the values in Table 2 are best explained by time-dependent proton-transfers from the bridging carbon to the 4-position of the organolithium reagent generated (Equation 27).

$$
\begin{align*}
\text{H} & \quad \text{H} \\
58 & \quad 30
\end{align*}
$$

Intuitively, it might be anticipated that $30$ would be more stable than $58$ due to conjugation with the aromatic nucleus.

This reaction though interesting limits use of the organo-metallic in a synthetic sequence and explains the complexity of the previous reaction mixtures. It is likely that the more covalent Grignard reagent undergoes
TABLE 2
POSITION OF DEUTERIUM LABEL UPON QUENCHING
4-LITHIO-1H-CYCLOBUTA[de]NAPHTHALENE (58) AT
VARIOUS TIME INTERVALS WITH D$_2$O.

\[
\begin{align*}
\text{Br} & \quad \text{1. BuLi} & \quad \text{D} & \quad \text{2. D}_2\text{O} \\
\text{D} & \quad \text{D} & \quad \text{D} & \\
\text{Time (min)}^a & \quad \text{Percentage of Each Component}^b \\
2 & 91 & 9 & 0 \\
10 & 80 & 15 & 5 \\
20 & 65 & 26 & 9 \\
30 & 54 & 35 & 11 \\
\end{align*}
\]

$^a$Length of time organo-metallic existed at -78$^\circ$ before deuteration.

$^b$Values obtained by nmr and mass spectral analysis.
the rearrangement slower. With precisely controlled conditions the Grignard reagent could prove useful.

**Free Radical and Carbonium Ion Chemistry**

The generation, stability, and use of various intermediates at the bridging carbon is an important aspect of 1H-cyclobuta[de]naphthalene chemistry. Card studied the carbanion at C-1 of 1 and also touched on the free radical and carbonium ion. His carbanion work revealed the methylene hydrogens of 1 to be considerably less acidic than the corresponding hydrogens of fluorene (59) and diphenylmethane (60) and still less acidic than those of acenaphthene (49). The pK\textsubscript{a} of 1 is probably near that of toluene. The lowered conjugative stability (originally expected to be in the range of the similar structures 59 and 60) is probably due to the strain in 61 limiting the delocalization as in Equation 28.

\[
\begin{align*}
\text{H} & \quad \leftrightarrow \quad \text{H} \\
\text{C}_{\text{H}} & \quad \leftrightarrow \quad \text{C}_{\text{H}} \\
\text{etc.} & \quad \leftrightarrow \quad \text{etc.}
\end{align*}
\]

A purpose of the present investigation is to determine the chemistry of free radicals and carbonium ions at the bridging carbon of cyclobuta[de]naphthalenes.
Addition of hydrogen bromide to bridged olefins 22, 23, 24, and 25 gives information as to the relative ease of formation of carbonium ions at C-1 in cyclobuta[de]-naphthalenes as compared to primary, secondary, tertiary, and benzylic carbonium ion moieties. Experimentally, hydrogen bromide is condensed into a solution of the desired olefin in methylene chloride at -78° wherein the reaction reaches completion in several hours. The products appear to be of kinetic control since the compositions do not vary with reaction time and temperature (from -78° to 25°). Table 3 illustrates that the carbonium ion on the peri-bridge carbon is generated more rapidly and presumably is significantly more stable than primary, secondary, tertiary, and benzylic carbenes. Only for olefin 24 is a minor product detectible probably meaning the tertiary ion is closer in energy to the C-1 ion than the other examples. This result is also in general agreement with the known greater stabilities of tertiary over benzylic carbonium ions.15

1-Bromo-1-ethyl-1H-cyclobuta[de]naphthalene (63) is identified by its exact mass and spectral characteristics, notably a nmr triplet at δ 1.23 and a quartet at δ 2.50. Bromides 64 and 65, though inseparable, display important
TABLE 3

PRODUCTS OF HYDROGEN BROMIDE ADDITION TO OLEFINS 22, 23, 24, AND 25.

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Image of olefin 22]</td>
<td>![Image of product 62]</td>
</tr>
<tr>
<td>![Image of olefin 23]</td>
<td>![Image of product 63]</td>
</tr>
<tr>
<td>![Image of olefin 24]</td>
<td>![Image of products 64 and 65]</td>
</tr>
<tr>
<td>![Image of olefin 25]</td>
<td>![Image of product 66]</td>
</tr>
</tbody>
</table>

\(^a\)This reaction was performed by Card (Ref. 6).
nmr absorptions of δ 1.27 (doublet) and 2.30 (septet) for the major product (64) and δ 1.83 (singlet) and 5.69 (singlet) for the minor (65). Additional spectra combined with exact mass and chemical origin corroborates the structural assignments given these adducts. The benzylic singlet at δ 3.83 in the nmr of 66 is its most distinctive feature. Again, exact mass and spectra give unequivocal proof of structure and the homogeneity of 66.

Pursuant to comparing the ease of generation of a 1H-cyclobuta[de]naphthalen-1-yl carbonium ion to its benzhydryl ion (Φ₂⁺) counterpart, it was necessary to synthesize 1-(diphenylmethylene)-1H-cyclobuta[de]-naphthalene (67, Equation 29) via Wittig reaction of the phosphorane from 20 and benzophenone. The procedure developed is a modification of that used previously to prepare 22, 23, 24, and 25. The Wittig reaction is noticeably slower with benzophenone requiring 24 hr at 65° for a 70% yield, while olefins 22 to 25 give excellent yields (~85%) in a few hours at room temperature. The fact that the reaction works well with benzophenone
demonstrates the extreme reactivity of 1H-cyclobuta[de]-naphthylidene-1-triphenylphosphorane (21).

Addition of hydrogen bromide to 67 produces an unusual result (Equation 30) as the carbon skeleton rearranges. 1,2-Diphenylacenaphthylene (68) is produced almost quantitatively as a characteristic orange solid (mp 161-163°, lit16 162-163°). The mechanism of rearrangement probably involves protonation, ring expansion, phenyl migration, and finally loss of proton to give 68 (Equation 31). Prior to evaporation of the hydrogen bromide, the reaction mixture displays a dark blue color characteristic of carbonium ion 69.16 1,2-Diphenylacenaphthylene (68) does not add hydrogen bromide under the reaction conditions used.
The reaction to give 68, though not giving the normal addition product, does seem to indicate that the diphenyl carbonium ion is more easily generated and more stable than the C-1 carbonium ion.

Card has prepared epoxide 70 and effected its rearrangement to ketone 33 and 2-methylacenaphthenone (71, Equation 32) with boron trifluoride. This reaction of excess boron trifluoride-etherate with 70 in methylene chloride for 5 minutes at room temperature produces 33 and 71 in a ratio of 1 to 7. The mechanism proposed involves opening of the epoxide in both possible directions (Equation 33).
In view of the result of hydrogen bromide addition to olefin 23, which shows that the C-1 carbonium ion is generated rather than the secondary ion, the mechanism in Equation 33 seemed questionable.

A milder procedure (treating epoxide 63 with boron trifluoride-etherate in a large volume of diethyl ether at -30° for several hours) does indeed produce ketone 33 as the sole product (Equation 34).

\[ 70 \xrightarrow{BF_3} 33 \xrightarrow{BF_3} 71 \]  

(34)

The reaction requires precise control of conditions and if deliberately continued for a long period of time ketone 33 rearranges to 71. The mechanism of rearrangement of 33 is thus simply coordination of the Lewis acid

\[ O - BF_3 \]

with the carbonyl, ring expansion, and finally methyl migration (Equation 35).

\[ \xrightarrow{BF_3} \xrightarrow{-BF_3} 71 \]  

(35)
A convenient synthesis of valuable ketone \[33\] is now available (see Chemistry At The Bridging Carbon chapter).

The \(1\)H-cyclobuta[de]naphthalen-1-yl radical \[29\] is also an interesting species. Bromide \[4\] can be regenerated (~80%) from hydrocarbon \[1\] using N-bromosuccinimide and a free radical initiator (Equation 16).

\[
\text{Initiation: } R^* + R'_2\text{CH}_2 \rightarrow R-H + R'_2\text{CH}. \\
\text{Propagation: } R'_2\text{CH}^* + \text{N-Br} \rightarrow R'_2\text{CHBr} + \text{N}^* \\
\text{Termination: } R^* + R^* \rightarrow R-R
\]

Scheme 2

The basic mechanism\(^{17}\) for bromination by N-bromosuccinimide (Scheme 2) illustrates the importance of the initiation step. The actual bromination takes place in a propagation step. Though the reaction works well on \(1\) it is noticeably slower and trickier to initiate than with fluorene \(59\), probably because radical \(29\) is less stable than the corresponding fluorenyl radical. Reaction of nitro compound \(42\) with N-bromosuccinimide under similar conditions fails. The nitro group may be intercepting the initiator radicals and preventing the reaction.
Attempts to synthesize 1,1-dibromo or 1-bromo-1-chloro-1H-cyclobuta[de]naphthalene (72) fail when N-bromosuccinimide or N-chlorosuccinimide and initiators are reacted with bromide 4. It is difficult to prepare gem-dihalogen compounds in this manner as electron-withdrawing groups (even a mild one like bromine) on the desired reaction site retard abstraction of the benzylic hydrogen.\textsuperscript{17} This phenomena may be a combination of electrostatic and steric interactions.

Use of the more vigorous reagent, tertiary butyl hypochlorite, produces excellent (89%) yields of 72. Bromochloride 72 is a white crystalline solid (mp 104-106°) whose spectral characteristics (particularly a 7-line C\textsuperscript{13} nmr), exact mass, and elemental analysis provide supportive evidence of its structure (see Chemistry at the Bridging Carbon chapter for chemistry of 72).

Hydrogen bromide can be easily added to olefin 23 free radically (Equation 37). The sole product,
1-(1-bromoethyl)-1H-cyclobuta[de]naphthalene (74), reaffirms the stability order developed in the previous hydrogen bromide heterolytic additions. The free radical at C-1 (73) is obviously formed faster than the secondary radical, paralleling the carbonium ion order. More importantly for the purposes of synthesis, the two modes of addition, homolytic and heterolytic, allow absolute control of the position of functionality thus are quite useful. Bromide 74, whose nmr provides the major source of information for its structural assignment, displays a large doublet (methyl) at δ 1.78, a doublet (bridge) at δ 5.40, and a doublet of quartets (proton α to bromine) at δ 4.38. Exact mass, combustion analysis, and other spectral absorptions are consistent with 74.

One of the most unusual reactions of the 1H-cyclobuta[de]naphthalene system is photobromination. Hydrocarbon 7 when photolyzed (100 watt bulb) with 1 eq of bromine in carbon tetrachloride and then column
chromatography on silica gel gives 1α,2β,3β,4α-tetra-bromo-1α,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (75, 39%, Equation 38) along with recovered 1 (36%).

None of the free radical substitution product 4, with a bromine on the bridge carbon, is seen. Under the same conditions naphthalene 52 is known to give a corresponding tetrabromide, but hydrocarbon 1 is one of the few aromatic molecules with benzylic hydrogens not to brominate at the benzylic position. Acenaphthene (49), fluorene (59), various methyl and dimethylnaphthalenes, and of course toluene readily photobrominate at their alpha positions. These hydrocarbons also give the bromides with N-bromosuccinimide under free radical conditions, whereas 1 yields different products with N-bromosuccinimide and by photobromination.
The bromine radicals generated by photolysis do not abstract either of the two benzylic hydrogens but do add readily to the highly strained ring system of hydrocarbon \( 1 \).

Tetrabromide \( 75 \), which crystallizes into "perfect" white cubes of mp 119-121\(^\circ\), is identified as a single compound (racemic) primarily by its sharp nmr (see Spectra chapter for a detailed discussion of the stereochemical elucidation). Additional spectra, exact mass, and combustion analysis give confirmation of the assigned structure.

Though the photobromination of naphthalene derivatives is well documented the best references on mechanism and stereochemistry concern the photochlorination of naphthalenes.\(^{23-26}\) At low temperature \( 76 \) can be isolated,

\[
\begin{align*}
\text{52} & \xrightarrow{\text{Cl}_2, \text{hv}} \text{Cl} \quad \text{Cl} \\
\text{76} & \xrightarrow{\text{Cl}_2, \text{hv}} \text{Cl} \quad \text{Cl} + \text{Cl} \\
\text{77} & \text{major} \\
\text{78} & \text{(39)}
\end{align*}
\]
thus connotating 1-2 and not 1-4 addition. Further chlorination produces \textit{trans-cis-trans} structure \textit{77} as the predominating product, the all \textit{trans} (\textit{78}) being the minor product (Equation 39).

A number of stereoisomers are possible, but since all naphthalenes undergo \textit{trans} photoaddition across a double bond only two products are obtained (other than in trace quantities). \textsuperscript{23-26}

Assuming that the same mechanism applies for photo-bromination as photochlorination, bromine radicals probably add \textit{trans} across the 3-4 bond of \textit{1} (opposite the cyclobutyl ring) as this is the weakest aromatic bond. The addition across the remaining 1a-2 double bond also in a \textit{trans} manner should be rapid, as the initial loss of aromaticity likely is the slow step. The assigned structure (\textit{75}) contains a \textit{trans-cis-trans} relationship of the bromine atoms, where \textit{trans-trans-trans} might have been expected as at least a minor product. The further constraint from the cyclobutane ring in \textit{1} compared to naphthalene seems to favor the \textit{trans-cis-trans} epimer exclusively. Because of the severe twisting necessary in the cyclohexane ring the least steric interaction between the bromines is possible with the \textit{trans-cis-trans} structure. Reaction of tetrabromide \textit{75} with the hindered
base, 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), causes rapid double-dehydrobromination (Equation 40). The reaction is specific since only 2,4-dibromo-1H-cyclobuta-[de]naphthalene (79) forms.
A number of mechanisms can be visualized to account for this product. Removal of the 4-proton (probably the most acidic) and eliminating the 3-bromine (path a) or removal of the 2-proton and eliminating the 1a-bromine (path b) are both cis eliminations with the second dehydrobromination also being cis. Removal of the 2-proton and loss of the 3-bromine is a trans elimination; the second step would be a trans 1-4 elimination (path c). Other mechanisms appear unlikely as they would give rise to unobserved products.

Spectral absorbances, exact mass, and elemental analysis lend credence to the assigned structure of 79. The most notable feature is an isolated aromatic nmr singlet at $\delta$ 7.20 for the 3-hydrogen. The ortho (or 7) proton is at $\delta$ 6.98-7.07 and the remaining meta and para hydrogens are a multiplet at $\delta$ 7.38-7.46. The methylene bridge is an obvious singlet ($\delta$ 4.63).

Tetrabromide 75 is the first example of a new ring system with two six-membered rings (one saturated, the other unsaturated) joined to a cyclobutane ring. In an attempt to prepare the parent hydrocarbon 80 by reduction Red-Al was reacted with 75 (Equation 41).
The desired hydrocarbon \(80\) is not obtained; instead the familiar unsaturated hydrocarbon \(1\) is produced in almost quantitative yield. It is possible that \(80\) is formed but rapidly aromatizes to \(1\). A better alternative is that the displacements of the bromines are quite slow so Red-Al acts as a base and double dehydrobrominates \(75\) instead. The product, probably \(79\), is then unstable to excess Red-Al which removes aromatic halogens. In a separate reaction Red-Al does change dibromide \(79\) into hydrocarbon \(1\) which is in agreement with the second part of the proposed mechanism.

Reactions on tetrabromide \(75\), though the parent hydrocarbon \(80\) is not formed, do produce the first member of the \(1H\)-cyclobuta[de]naphthalene system with an \textit{ortho} substituent \((79)\). The synthetic utility of the \textit{ortho} substituent is unexplored to date.

Photobromination of bromide \(4\) gives pentabromides \(81a,b\) (36%, Equation 42) of presumed stereochemistry in a ratio of 4:1. Fractional crystallization partially
separates the two isomers. The major compound is tentatively assigned 1,1α,2β,3α,4β-pentabromo-1a,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (81a), while the minor is 1,1α,2β,3β,4α-pentabromo-1a,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (81b, see Spectral chapter for stereochemical assignment). The minor isomer has the same relationship of its four cyclohexylbromines as does 75 (trans-cis-trans), but the major isomer possesses a trans-trans-trans arrangement. The stereochemistry of the bridge bromine is not known, but considering the difference in the products of photobromination of 1 and 4 obviously the C-1 bromine exerts a significant steric effect. It is likely that the 1-la bromines are trans for both the major and minor products.

The structures of 81 are supported by spectra, exact mass, and combustion analysis. The minor product crystallizes from a solution of both isomers; each isomer
forms stable white cube-like crystals of identical melting points (144-146°).

Reaction of $\text{81}$ with zinc in ether containing a trace of acetic acid regenerates bromide $\text{4}$ ($\sim 90\%$) and a small amount of hydrocarbon $\text{1}$ (Equation 43).

\[
\begin{align*}
\text{81} & \xrightarrow{\text{Zn}} \text{4} \\
\text{81} & \xrightarrow{\text{DBU}} (\text{84a, b, 80\%}, \text{Equation 44}). \text{ Dibromides 84a, b are two inseparable}
\end{align*}
\]

One mode of reaction would give highly strained intermediate $\text{82}$ and then probably $\text{83}$. This desirable pathway, which would also be a synthetic route to an ortho-substituted peri-bridged naphthalene, is not observed since pentabromide $\text{81}$ undergoes the more straightforward reaction to $\text{4}$.

DBU(1,5-diazabicyclo[5.4.0]undec-5-ene) readily dehydrobrominates $\text{81}$ to two dibromides ($\text{84a, b, 80\%}$, Equation 44). Dibromides $\text{84a, b}$ are two inseparable
geometric isomers. The exact structures could not be determined but are most probably the 1,2,4- and 1,2,3-tribromides. The nmr absorbances at δ 6.63 and 6.70 for the bridge protons of the two isomers indicate that the dibromides are present in approximately equal amounts. Exact mass and combustion analysis give further evidence of the general structures of 84a,b. The fact that there are two compounds 84a,b indicates that the bridge bromine atom affects the mode of elimination as compared to that of tetrabromide 75.

Chemistry at the Bridging Carbon

Chemistry centering around the C-1 bridging carbon is probably the most significant and interesting of the 1H-cyclobuta[de]naphthalenes.

Gem-dihalides are chemical analogs of carbonyl compounds as both functionalities undergo many of the same reactions. Since bridged ketone 26 ring-opens easily, bromochloro compound 72 was studied in the anticipation that it would be a synthon of 26 that does not ring-open.
Hydrolysis of 72 with potassium hydroxide in a water-tetrahydrofuran mixture proceeds slowly. The desired ketone 26 is not obtained but potassium 1-naphthoate is formed under the reaction conditions (Equation 45). It is possible that 26 is formed but undergoes rapid hydrolytic ring-opening.

\[
\begin{align*}
\text{Br} & \quad \text{Cl} \\
\text{72} & \quad \text{KOH} \\
\text{CO}_2\text{K} & \quad \text{(45)}
\end{align*}
\]

Reactions of 26 with various amines and with hydrazines do not give the expected ketone derivatives. For instance, reaction with aniline gives 1-naphthanilide (85) probably via rearrangement of intermediate hemiaminal 86 (Equation 46).

\[
\begin{align*}
\text{26} & \quad \phi\text{NH}_2 \\
\text{86} & \quad \phi\text{NH}_2 \\
\text{85} & \quad \phi\text{NH}_2
\end{align*}
\]

In an attempt to circumvent these rearrangements 72 was reacted with hydrazines. Surprisingly, the desired derivatives (carbene precursors) do not form. p-Toluenesulfonyl hydrazide in methanol and tetrahydrofuran when
refluxed 24 hr with 72 gives hydrocarbon 1 and methyl 8-bromo-1-naphthoate 87 in respective yields of 29% and 10% along with unreacted 72 (35%) (Equation 47).

\[ 72 \xrightarrow{H_2NNH_2} 1 + 87 \quad (47) \]

The identity of 1 is easily confirmed by nmr and mass spectroscopy. Its formation is probably due to a pseudo-Wolf-Kishner reduction.

A complicated mechanism is needed to account for ester 87. A possible explanation is that first the p-toluenesulfonylhydrazide displaces the bromine forming hydrazine intermediate 88. The bromide ion then attacks the cyclobutyl ring giving anion 89 which rapidly displaces p-toluensulfinate to produce diaziridine 90. Methanolysis of the side chain would give observed ester 87. The structure of 87 is demonstrated by molecular
ion peaks at 264 and 266 and large peaks at 233 and 235 (loss of methoxy radical) in the mass spectrum. The infrared reveals a carbonyl (1720 cm\(^{-1}\)) while the nmr has a significant singlet at \(\delta 3.85\) (methyl of ester); both absorbances and tlc match an authentic sample.

Reaction of bromochloride 72 with hydrazine in tetrahydrofuran yields 1-naphthaldehyde azine (91, 21%) and 9-bromo-3H-benz[e]indazole (92, 12%, Equation 49).

\[
\begin{array}{c}
\text{72} \xrightarrow{\text{H}_2\text{NNH}_2} \text{91} \quad \text{92}
\end{array}
\]

No simple mechanism can account for 91 or 92. Displacement of the bromine by hydrazine gives 93 which by elimination of hydrogen chloride produces hydrazone 94. Dimerization and ring-opening of 94 should yield 95 which would readily lose nitrogen forming the azine product 91 (path a, Equation 50). Bromide ion ring-opening of 93 and proton abstraction gives hydrazine 96. Loss of hydrogen chloride to hydrazone 97 and oxidation to diazo compound 8 accounts for 92, since 8 thermally decomposes to 92 (path b, Equation 50).³
Attempts to prepare ketal 98 by either methanolation (with methanol and sodium methoxide) or reaction of 72 with silver nitrate (a dilute solution in methanol) give good yields of methyl 1-naphthoate (99). Ketal 98 may have been formed but cleaves in the presence of excess methanol to 99 possibly via ortho ester 100 (Equation 51).
Refluxing zinc-silver couple with bromide 4 in water provides 1,1'-bi-1H-cyclobuta[de]naphthalene (101, 65%) along with reduction product 1 (11%, Equation 52).

\[
\begin{align*}
4 & \xrightarrow{\text{Zn-Ag}} \quad \begin{array}{c}
\text{101} \\
\text{102}
\end{array} \\
& + 1
\end{align*}
\] (52)

Coupled product 101 is a needle-like solid (mp 135-137\(^\circ\)) whose structure is consistent with its spectra, exact mass, and combustion analysis. The 7 line C\(^{13}\) nmr of 101 gives convincing proof of a symmetrical structure. The bridge hydrogen exhibits a sharp proton nmr singlet at 6 5.80.

Thermal rearrangement of 101 at 430\(^\circ\) produces 1-(1-naphthylidene)-1H-cyclobuta[de]naphthalene (102, Equation 53). The mechanism possibly involves fission of one cyclobutane ring to a diradical, then hydrogen transfer to form olefin 102. Further heating of 102 may yield 1,1'-dinaphthylacetylene (Equation 12).
Identification of 102 is made difficult by the fact that its olefinic hydrogen is buried in the aromatic region of the nmr. Independent synthesis of 102 is accomplished, however, by reaction of 1-naphthaldehyde with the Wittig reagent from phosphonium salt 20 (Equation 54).

\[
\begin{align*}
\text{Br}^+ & \quad \Phi_3P \\
\quad & \quad \\
\text{20} & \quad \text{1) } t-\text{BuLi} \\
\text{102} & \quad \text{2) CHO}
\end{align*}
\]

Both samples of 102 display identical melting points (107-109\°C) and spectra, including the fine structure in the aromatic region of the nmr. Titration of 102 with a dilute solution of bromine in carbon tetrachloride reveals the presence of only one equivalent of unsaturation.
by uptake of one equivalent of bromine, thus eliminating the possibility of 102 being 1,1'-dinaphthylacetylene (Equation 55).

\[
\begin{align*}
102 & \quad \text{Br}_2 \quad \rightarrow \\
& \quad 103
\end{align*}
\]

Confirmation of the structure of dibromide 103 comes from spectral, exact mass, and elemental analyses. The most significant nmr feature is a singlet at δ 6.69 representing the benzylic hydrogen. The resonance is clearly separated from the aromatic protons at δ 6.85-8.2.

Bromochloride 102 reacts with silver-activated zinc in tetrahydrofuran to form Δ1,1'-bi-1H-cyclobuta[de]-naphthalene (104) in a yield of 29% with hydrocarbon 1 as a minor product (14%, Scheme 2). An alternate synthesis of 104 involves the monochlorination of 101 and then treatment of the crude chloride 105 with either DBU(1,5-diazobicyclo[5.4.0]undec-5-ene) or lithium diisopropylamide (respective overall yields of 21% and 24%).
Scheme 2

Olefin 104 is surprisingly stable at room temperature and identified by its spectral absorptions, exact mass, and combustion analysis. Its $^{13}$C nmr consists of 7 lines revealing the symmetry of 104.

The chemistry of olefin 104 is as yet virtually unexplored due to the difficulty in obtaining it pure. The zinc synthesis of 104 is by far the method of choice since it gives higher yields and greater reproducibility. Complications in the preparation of this unique molecule (104) are the lack of repeatability in generating the zinc-silver couple and the fact that there are minor
products (probably higher molecular weight material and halogen containing compounds) that impart separation problems.

Previous studies have shown the high reactivity of olefins 22, 23, and 24 to addition. It was decided, therefore, to investigate the Diels-Alder reactions of these molecules.

Refluxing 1-methylene-1H-cyclobuta[de]naphthalene (22) with tetraphenylcyclopentadienone in xylene produces 1',4',5',6'-tetraphenylspiro[1H-cyclobuta[de]-naphthalene-1,2'-[5]norbornen-7'-one (106, 69%, Equation 56). A carbonyl ir absorption at 1760 cm\(^{-1}\) and a satisfactory combustion analysis are consistent with the structural assignment of 106. Ketone 106 displays several unusual spectral features. The nmr contains only a large multiplet at \(\delta\) 6.65-8.0. The methylene
protons are deshielded into the aromatic region by the naphthalene moiety. The mass spectral molecular ion (536) of 106 is a very small peak; loss of carbon monoxide in the mass spectrometer leads to a huge 508 peak; in agreement with the structural assignment.

Ethylidene 23 and isopropylidene 24 analogs fail to react with tetraphenylcyclopentadiene in xylene. Steric factors caused by the methyl groups of 23 and 24 may prevent the Diels-Alder reactions from being viable.

1-methylene-1H-cyclobut[a]naphthalene (22) undergoes cyclopropanation by methylene iodide and zinc/copper couple (Equation 57) to give spiro[1H-cyclobuta[a]naphthalene-1,1'-cyclopropane (107, 82%) as assigned from its spectra, combustion analysis, and exact mass. The proton nmr contains the expected absorptions at δ 1.53 (s, 4H, CH2), 6.88 (d of d, 2H, J = 2Hz and 4Hz, ortho) and 7.4-7.65 (m, 4H, meta and para).

One of the major goals of the present research is to develop methods of carbon-carbon bond formation from
the C-1 bridging carbon of the 1H-cyclobuta[de]naphthalene system. Success in this area would lead to unusual derivatives for possible advantageous chemistry.

Card\(^6\) has previously reported that reaction of bromide 4 with cyanide ion fails. Thus bromide 4 and potassium cyanide in refluxing acetonitrile containing a trace of 18-crown-6 ether produces a mixture of virtually inseparable compounds. It has now been found that displacement using cyanide ion occurs efficiently under special conditions. Stirring bromide 4 with potassium cyanide in acetonitrile and an equivalent of 18-crown-6 ether for 12 days at room temperature gives 1-cyano-1H-cyclobuta[de]naphthalene (108, 85%, Equation 58).

\[
\begin{align*}
4 \quad &\xrightarrow{\text{KCN}} 108 \\
\end{align*}
\]

Use of a smaller amount of the crown ether (5-10% equivalents) retards the displacement to an imperceptible rate. The structure of 108 is derived from its exact mass, combustion analysis, and spectra. The infrared
exhibits a prominent nitrile peak at 2250 cm\(^{-1}\) and the 7 line C\(^{13}\) nmr of 108 (disregarding the nitrile carbon) is consistent with its symmetry.

Nitrile 108 is saponifiable to 1H-cyclobuta[de]-naphthalene-1-carboxylic acid (109, 32%, Equation 59).

\[
\begin{align*}
108 & \xrightarrow{\text{1)} \Theta, \text{OH}} 109 \\
& \xrightarrow{\text{1)} \text{MeMgBr}, \text{2)} \text{HCl, H}_2\text{O}} 33
\end{align*}
\]

Reaction of 108 with methyl magnesium bromide and subsequent hydrolysis gives an alternate synthesis of ketone 33 (Equation 59). The unsatisfactory yield (18%) may be due to the acidic C-1 proton discharging the Grignard reagent since reaction of 108 with methyllithium produces only the C-1 carbanion and no addition product. It is also possible that the hydrolysis step does not proceed smoothly.
A study was then undertaken of the relative kinetic acidities of nitrile 108 and similar molecules - 9-cyanofluorene (110) and diphenylacetonitrile (111). The nitriles were mixed with a standard solution of triethylamine in t-butanol-0-D and the deuterium incorporation at various time intervals was monitored by nmr. The rate of deuterium exchange follows the order of 110 > 111 > 108 with approximate rates of 600-12-1 (comparing the times needed to reach 50% deuteration, see Table 4). 9-Cyanofluorene (110) is the fastest because of acidifying electronic factors and because its fused aromatic rings are held rigidly coplanar. Steric hindrance to removal of the acidic hydrogen in 110 is small and the planar structure of its conjugate carbanion allows extensive conjugative delocalization through the fluorene moiety and the cyano group. Diphenylacetonitrile (111) must incur much larger steric hindrance in removal of its cyano proton and in stabilization of the resulting anion. The phenyl groups are not held rigidly and do not become planar readily. Though the C-1 bridge proton of 1-cyano-1H-cyclobuta[de]naphthalene (108) is accessible for removal by the base, 108 is the slowest of the present series because extensive resonance stabilization at the
### TABLE 4

**RELATIVE RATE OF DEUTERIUM EXCHANGE ON 9-CYANOFLUORENE (110), DIPHENYLACETONITRILE (111) AND 1-CYCLOBUTA[de]NAPHTHALENE (108).**

<table>
<thead>
<tr>
<th>Time</th>
<th>Percentage of Deuteration&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0</td>
</tr>
<tr>
<td>1 min</td>
<td>10</td>
</tr>
<tr>
<td>3 min</td>
<td>15</td>
</tr>
<tr>
<td>5 min</td>
<td>21</td>
</tr>
<tr>
<td>10 min</td>
<td>30</td>
</tr>
<tr>
<td>25 min</td>
<td>34</td>
</tr>
<tr>
<td>40 min</td>
<td>37</td>
</tr>
<tr>
<td>1 hr 15 min</td>
<td>45</td>
</tr>
<tr>
<td>4 hr</td>
<td>60</td>
</tr>
<tr>
<td>6 hr</td>
<td>68</td>
</tr>
<tr>
<td>20 hr</td>
<td>88</td>
</tr>
<tr>
<td>40 hr</td>
<td>96</td>
</tr>
<tr>
<td>75 hr</td>
<td>44</td>
</tr>
<tr>
<td>150 hr</td>
<td>57</td>
</tr>
<tr>
<td>190 hr</td>
<td>77</td>
</tr>
</tbody>
</table>

<sup>a</sup> The reaction was effected in t-butanol-OD using triethylamine as the base.

<sup>b</sup> The rate of reaction was monitored by nmr.
C-1 anion involves a highly strained cyclobutadiene-like delocalization.

To test the mild procedure for difficult nucleophilic displacements (using a large amount of crown ether and room temperature for several weeks) of bromide 4, reaction with nitrite ion, an ambident nucleophile, was investigated. On treating 4 with potassium nitrite in acetonitrile and 18-crown-6 ether for 2 weeks, only one product is isolated, 1-naphthaldehyde (41, 72%, Equation 60). 1-Naphthaldehyde is also produced if the mixture is refluxed 2 hours.

\[
\begin{align*}
4 + \text{KNO}_2 &\rightarrow \begin{array}{c}
\text{H} \\
\text{ONO}
\end{array} & \rightarrow \begin{array}{c}
\text{H} \\
\text{O}.
\end{array} & \rightarrow \begin{array}{c}
\text{H} \\
\text{CHO}
\end{array}
\end{align*}
\]

Aqueous or non-aqueous workup does not alter the product obtained. It is apparent that the nitrite ion attacks as an oxygen nucleophile here and not as a nitrogen nucleophile. It is presumed that the nitrite ester intermediate is unstable, losing nitric oxide to give an alkoxy radical that rearranges with abstraction of a proton from the solvent to give 1-naphthaldehyde (41).
In a continuing effort to develop methods of carbon-carbon bond formation, various cuprate reagents were reacted with 1-halo-1H-cyclobuta[de]naphthalenes. The product of lithium dimethyl cuprate with halides \(1\text{H2}, \text{4}, \text{16}, \text{19}\), and tosylate \(1\text{9}\) is 1-methyl-1H-cyclobuta[de]-naphthalene (32, Equation 61). The respective yields of \(\text{32}\) from \(\text{1H2}, \text{4}, \text{16}, \text{19}\) are 13\%, 10\%, 6\%, and 71\%.

Halides \(\text{1H2}, \text{4}, \text{16}\) give low rather useless yields of the alkylation product and much intractable material. The cuprate reaction on tosylate \(\text{19}\) works well and indicates promise for other cuprate reagents in the future.

Intermediates \(\text{4}, \text{16}, \text{19}, \text{32}\) have been prepared previously.\(^3\)\(^6\) In the present investigation 1-chloro-1H-cyclobuta[de]naphthalene (112) was obtained from 4 by
displacement with potassium chloride in refluxing acetonitrile and a trace of 18-crown-6 ether or by reaction with benzyltriethylammonium chloride in chloroform (respective yields of 89% and 92%, Equation 62).

\[
\begin{align*}
\text{KCl, CH}_3\text{CN} & \quad \text{or} \\
\Theta & \quad \Theta \\
\text{H},\text{H} & \quad \text{Cl}
\end{align*}
\]

1-Chloro-1H-cyclobuta[d]naphthalene (112) is a white solid (mp 65-67°) whose exact mass, combustion analysis, and spectra (including a 7 line C\textsuperscript{13} nmr) confirm its structure.

Tosylate 19 is produced in 45% yield from bromide 4 and silver tosylate in hexamethylphosphoramide (75°, 50 hr). A significant improvement in yield (67%) is accomplished by using 1.5 eq of silver tosylate in hexamethylphosphoramide at 90° for 24 hr. Tosylate 19 will decompose to 1-naphthaldehyde (41) but prolonged heating seems to be more detrimental than does excess silver ion.

1-Vinyl-1H-cyclobuta[d]naphthalene (113) is of extreme interest because of its potential to undergo
thermal and/or photochemical isomerization to 1H-phenalene (114, Equation 63). Investigation of the synthesis of 113 was thus initiated.

\[ H \quad C = C H \]

113

Preparation of lithium divinyl cuprate by known methods\(^{27,28}\) and reaction with 1H-cyclobuta[de]-naphthalen-1-yl tosylate (19) fails, however, to give the expected vinyl compound 113 (Equation 64).

\[ \text{CuLi} \]

\[ H \quad C = C H_2 \]

19

\[ C = C H_2 \]

113

The product mixture is complex and no compound other than starting tosylate (119) can be identified.

1-Ethylidene-1H-cyclobuta[de]naphthalene (23) is a possible precursor to 113. The two isomers differ only
in position of their carbon–carbon double bonds. Base-catalyzed isomerization of 23 to 113 has been presently investigated.

Treatment of olefin 23 with t-butyllithium at -78° generates the expected allyl anion (115, Equation 65).

When anion 115 is quenched with deuterium oxide only 1-(ethylidene-2-d)-1H-cyclobuta[de]naphthalene (116) is formed. The alternate product, 1-deutero-1-vinyl-1H-cyclobuta[de]naphthalene (117) is not obtained. The absence of 117 reveals the importance of naphthalene conjugation with the double bond of the bridging atom even though highly strained and rules out synthesis of 1-vinyl-1H-cyclobuta[de]naphthalene (113) by base-catalyzed isomerization with relief of strain.
The evidence for 116 and hence for anion 115 is a large mass spectral peak at 167 for a monodeuterotero product. The nmr of 116, which for precursor 23 contains a doublet at δ 2.0 for the methyl group and a quartet at δ 5.8 for the vinylic proton, consists of a doublet at δ 2.0 integrating to only two hydrogens and a triplet at δ 5.8.

Bromide 74, prepared from free radical hydrobromination of 23, has the potential to be a precursor of vinyl compound 113. Reaction of bromide 74 with three highly hindered bases – 1,5-diazabicyclo[5.4.0]undec-5-ene, potassium triethylcarbin oxide, and lithium 2,2,6,6-tetramethylpiperidide – cleanly regenerates olefin 23; however, no 113 (Equation 66) is produced.
It is apparent that eliminative attacks occurs at the bridge proton to give strained olefin 23. It is unlikely that 113 is formed and then isomerizes to 23; amine and presumably alkoxide bases are too weak.

Ketone 33 also possesses the correct carbon skeleton to be a precursor for 113. 1-Acetyl-1H-cyclobuta[de]-naphthalene (33) reacts with p-tosylhydrazide to form the corresponding hydrazone (118, 69%), a white solid of mp 172-174° identified by its exact mass, elemental analysis, and spectra. The nmr absorptions of 118 are δ 1.76(s, 3H, ketone CH₃), 2.45(s, 3H, tosyl CH₃), 5.93 (s, 1H, bridge H), and 7.0-7.95(m, 10 H, aromatic).

Since reaction of alkyllithium (2 equiv) with a tosylhydrazone is a well-documented method of converting a ketone into an olefin, 29 118 was reacted with t-butyllithium (2 equiv) at -78° and stirred at room temperature for 24 hours to give 1-ethylidene-1H-cyclobuta-[de]naphthalene (23, Equation 67) in low yield (21%).
Surprisingly, the elusive vinyl compound 113 is not found. Whether 23 forms directly or 113 is formed and then isomerizes is unknown.

A promising route to 113 is conversion of 4 via t-butyl lithium and ethylene oxide (Equation 68) to 

![Chemical Structure](image)

1-(2-hydroxymethyl)-1H-cyclobuta[de]naphthalene (119) in 51% yield; hydrocarbon 1 is a minor product (18%). The structural assignment of 119 is based primarily on nmr absorbances at δ 1.96 (broad s, 1H, OH), 2.30 (q, 2H, J = 6Hz, CH₂ attached to bridge), 3.85 (t, 2H, J = CH₂, CH₂ near hydroxyl), 5.32 (t, 1H, J = 6Hz, bridge H), and 7.0-7.7 (m, 6H, aromatic). Other spectra including an infrared peak at 3100 cm⁻¹ (OH), exact mass, and combustion analysis give confirmation of the structure.

Alcohol 119 may be convertible to 1-vinyl-1H-cyclobuta[de]naphthalene (113) either by dehydration or conversion of its alcohol moiety to a halide or tosylate and subsequent elimination. Lack of material has made
study of these transformations impossible at the present time.

Spectral Properties of 1H-Cyclobuta[de]naphthalenes

Symmetrical 1H-cyclobuta[de]naphthalenes exhibit a characteristic pattern in the aromatic region of the proton nmr. The ortho protons appear as a doublet of a doublet in the area of $\delta$ 5.7-7.0, while the meta and para protons are a multiplet at $\delta$ 7.3-8.1. This multiplet exists primarily as a tall peak sided by two smaller ones (see Figure 4). This characteristic pattern, when applied to structure elucidation of the product of a new reaction, is a clear indication that the bridge (and thus the symmetry) of the 1H-cyclobuta-[de]naphthalene system has been retained.

Electron withdrawing substituents on the aromatic nucleus result in a substantial expansion of aromatic portion of the nmr. This effect allows a definite positional assignment of nitro compounds 42 and 44, and ketones 45 and 46. Figure 5 is a representation of the nmr spectrum of 4-nitro-1H-cyclobuta[de]naphthalene (42). Peaks 2 and 4 belong to proton 2 which is coupled (7 Hz)
Figure 4. Partial NMR of 1H-Cyclobuta[de]naphthalene (1).
Figure 5. Aromatic Splitting Pattern of 4-Nitro-1H-
cyclobuta[de]naphthalene (42).

to proton 3 whose absorbances are peaks 11 and 12.
Hydrogen 7 portrayed by peaks 1 and 3 is coupled (6 Hz)
to hydrogen 6 as is hydrogen 5 (peaks 9 and 10, $J = 9$ Hz).
Proton 6 is shown by a doublet of doublets (peaks 5, 6, 7,
and 8). The protons closest to the nitro group are
shifted away from tetramethyilsilane. No other substitu-
tion but the 4-position is consistent with this splitting
pattern.
Substituting an aromatic nucleus causes a change in the chemical shift of the proton nmr of benzylic hydrogens. Nitro groups affect the shift of 1H-cyclobuta[de]naphthalene less than for toluene and diphenylmethane, whereas bromine atoms induce a larger change for 1H-cyclobuta[de]naphthalene than for toluene (Table 5). Strangely, acetyl substitution shifts the benzylic hydrogens of 1H-cyclobuta[de]naphthalene upfield (opposite to the nitro group).

The ultimate tool for the structure elucidation of symmetrical 1H-cyclobuta[de]naphthalenes is C\text{13} nmr. The basic 1H-cyclobuta[de]naphthalene nucleus gives a seven signal spectrum. Figure 6 represents the C\text{13} nmr of 1-chloro-1H-cyclobuta[de]naphthalene (112). The resonance of the bridging carbon (peak 2) is of medium height while those of C_{2,7} (peak 4), C_{4,5} (peak 5), and C_{3,6} (peak 7) are enormous because they each represent two carbons. The resonances of quarternary carbons C_{9} (peak 6), C_{1a,7a} (peak 8), and C_{8} (peak 9) are small because of low Nuclear Overhauser Effects.\textsuperscript{34} The farther a carbon is from a hydrogen the lower the intensity of the signal, thus the absorbances of C_{9} and particularly C_{8} are
TABLE 5
CHEMICAL SHIFTS (δ) OF THE METHYL AND METHYLENE PROTONS OF SUBSTITUTED TOLUENES, DIPHENYLMETHANES, AND 1H-CYCLOBUTA[de]NAPHTHALENES.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>CH₃</th>
<th>R</th>
<th>CH₂</th>
<th>R</th>
<th>H</th>
<th>R'</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>2.29</td>
<td>3.89</td>
<td>31</td>
<td>4.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>H</td>
<td>2.45 (.16)</td>
<td>4.10 (.21)</td>
<td>32</td>
<td>4.73 (.04)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>NO₂</td>
<td>---</td>
<td>4.27 (.38)</td>
<td>32</td>
<td>4.81 (.12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-CH₃</td>
<td>H</td>
<td>2.32 (.03)</td>
<td>3.98 (.09)</td>
<td>33</td>
<td>4.53 (.16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>H</td>
<td>2.25 (.04)</td>
<td>---</td>
<td>---</td>
<td>4.50 (.19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>4.39 (.30)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values in parenthesis are the differences between the substituted molecules and parent hydrocarbons.*
Figure 6. The C$^{13}$ NMR of 1-Choro-1H-cyclobuta[de]naphthalene (112).
difficult to find in the spectrum of 1H-cyclobuta[de]-
naphthalenes. Peak 1 is from tetramethylsilane while
peak group 3 is from deuterochloroform. The small noisy
signals in the area of peaks 4 to 7 are the tall peaks
of impurities. Samples less than 95% pure are impractical.

The C\textsuperscript{13} signals in a spectrum of a 1H-cyclobuta[de]-
naphthalene derivative are relatively easy to assign
because the peaks, other than for the carbon containing
the functionality, change only minimally from compound to
compound (Table 6). Chloride \textsuperscript{112} and dibromide \textsuperscript{48} are
two of the few molecules of this system whose \textsuperscript{C_8} shift
is greater than their \textsuperscript{C_{1a,7a}} shift. Coupled product \textsuperscript{104}
and olefin \textsuperscript{22} correspond quite closely except for the
shift of \textsuperscript{C_{1a,7a}}. 4,5-Dinitro-1H-cyclobuta[de]naphthalene
(\textsuperscript{43}) exhibits some unusual C\textsuperscript{13} nmr shifts. The resonance
of carbons 4 and 5 to which the nitro groups are attached
shift downfield though surprisingly not past \textsuperscript{C_{1a,7a}}.
Carbon 9 \textit{ortho} to both nitro groups is moved considerably
toward tetramethylsilane. Carbons \textit{ortho} to aromatic
nitro groups are known to shift upfield.\textsuperscript{35}

The most difficult structural assignments in this
study involve tetrabromide \textsuperscript{75} and pentabromides \textsuperscript{81a,b}.
The stereochemistry of these molecules can best be
### TABLE 6

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{C}^1 )</th>
<th>( \text{C}_{2,7} )</th>
<th>( \text{C}_{4,5} )</th>
<th>( \text{C}_9 )</th>
<th>( \text{C}_{3,6} )</th>
<th>( \text{C}_8 )</th>
<th>( \text{C}_{1a,7a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cl" /></td>
<td>66.1</td>
<td>115.9</td>
<td>123.0</td>
<td>126.3</td>
<td>131.3</td>
<td>195.3</td>
<td>143.7</td>
</tr>
<tr>
<td><img src="image" alt="Br" /></td>
<td>70.3</td>
<td>113.5</td>
<td>124.0</td>
<td>127.0</td>
<td>131.7</td>
<td>141.0</td>
<td>149.1</td>
</tr>
<tr>
<td><img src="image" alt="CN" /></td>
<td>45.7</td>
<td>117.3</td>
<td>123.3</td>
<td>126.1</td>
<td>131.1</td>
<td>137.0</td>
<td>146.4</td>
</tr>
<tr>
<td><img src="image" alt="H" /></td>
<td>65.0</td>
<td>116.4</td>
<td>121.7</td>
<td>125.7</td>
<td>130.3</td>
<td>144.4</td>
<td>145.5</td>
</tr>
</tbody>
</table>
Table 6 (continued)

<table>
<thead>
<tr>
<th></th>
<th>149.6</th>
<th>114.2</th>
<th>121.9</th>
<th>125.7</th>
<th>130.6</th>
<th>145.8</th>
<th>150.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>149.7</td>
<td>114.6</td>
<td>122.3</td>
<td>125.7</td>
<td>131.6</td>
<td>143.7</td>
<td>144.2</td>
</tr>
<tr>
<td>104</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.2</td>
<td>119.8</td>
<td>113.5</td>
<td>123.9</td>
<td>136.2</td>
<td>146.2</td>
<td>140.4</td>
</tr>
<tr>
<td>48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45.6</td>
<td>119.8</td>
<td>145.5</td>
<td>109.4</td>
<td>131.2</td>
<td>142.8</td>
<td>146.2</td>
</tr>
</tbody>
</table>

\[a\]The shift of carbon C-1' is omitted.
elucidated by analysis of their nmr spectra in the region of δ 4-5.5. The bridge protons of 75, though not identical, appear as a broad singlet (peak 1, Figure 7). Doublet of doublets 4 (J = 2.5Hz and 9Hz) can only belong to hydrogen 3. The large coupling constant (9Hz) of doublet 3 indicates a large dihedral angle (150-180°) and probably a trans diaxial arrangement of hydrogens.

Figure 7. Partial Proton NMR of Tetrabromide 75.
while the low coupling constant (2.5 Hz) of doublet 2 indicates a dihedral angle near 90° and a cis configuration. A \textit{trans-cis-trans} relationship of the bromine atoms (75) fits the data best: Proton 2 is cis to proton 3 and is doublet 2. Proton 4 which is trans to proton 3 is doublet 3. This assignment correlates perfectly with pentachloride 120 obtained from the photochlorination of 1-chloronaphthalene.23

\begin{equation}
\begin{align*}
J_{2,3} &= 2.5 \text{ Hz} \\
J_{3,4} &= 8.9 \text{ Hz}
\end{align*}
\end{equation}

The minor isomer of pentabromide 81 exhibits a splitting pattern in the proton nmr identical to that of tetrabromide 75 (Figure 8). Therefore, the stereochemistry of the minor isomer with regard to the four cyclohexyl bromines can be assumed to be identical to tetrabromide 75. Doublet 1 \((J = 2.5 \text{ Hz})\) represents proton 2 and doublet 2 \((J = 8 \text{ Hz})\) is proton 4 both of which are coupled to doublet of doublets 3, proton 3. The bridge proton is the sharp singlet 4 \((\delta 5.80)\).
Figure 8. Partial Proton NMR of Pentabromide 81b.
The major isomer (81a) displays a different pattern with larger coupling constants (Figure 9). Proton 3 is doublet of doublets 2 coupled to doublets 1 (11.5 Hz) and 3 (5 Hz). Singlet 5 represents the bridge proton while peak 4 is the bridge proton of the minor isomer (81b), an impurity here. A definite assignment of doublets 1 and 3 is not possible, though from the coupling constants doublet 1 would be a trans and probably diaxial interaction while doublet 3 could be

Figure 9. Partial NMR of Pentabromide 81a.
from a trans relationship not quite axial because of the severe twist of the cyclohexyl ring. A trans-trans-trans relationship of the four bromines on the 6-membered ring fits the spectral and chemical data best. Compound 121 is a similar structure isolated from the photochlorination of 1-chloronaphthalene.

\[ J_{2,3} = 11.6 \text{ Hz} \]
\[ J_{3,4} = 9.1 \text{ Hz} \]

Proton 2 of 81a can be assigned to doublet 1 and proton 4 to doublet 3 because for tetrabromide 75 and the minor isomer of 81 the 4 proton is shifted further downfield than proton 2. Also the coupling constant for the 2-3 protons of 121 correlate with this structure.

No information is available on the relative stereochemistry of the C1a bromine and the bridge bromine for either the major or minor isomer. The sharpness of the singlets for these protons indicates that there are only two compounds (not counting enantiomers) not the four possible.
The assigned structures of 75 and 81 are certainly not absolute considering the number of possible isomers and conformations. They do fit the data and seem quite reasonable.
EXPERIMENTAL

Melting Points. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are uncorrected.

Elemental Analyses. Elemental analyses were performed by Microanalysis, Inc., Wilmington, Del., or Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Infrared Spectra. Infrared spectra were obtained using Perkin Elmer Model 137 or 457 recording spectrophotometers. All spectra were calibrated against a polystyrene absorption peak at 1601 cm\(^{-1}\).

Proton Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra were determined using Varian Associates nuclear magnetic resonance spectrometers, Models A-60 and A-60A and a Bruker Model HX-90. Chemical shifts were measured in ppm downfield from tetramethylsilane unless otherwise indicated.

C\(^{13}\) Nuclear Magnetic Resonance Spectra. C\(^{13}\) nuclear magnetic resonance spectra were obtained using a Bruker Model HX-90 spectrometer, operating at 22.625 MHz and a Bruker Model HX-80 operating at 20.000 MHz. Chemical shifts were measured in ppm from tetramethylsilane.
Gas Chromatography. Gas chromatography was performed using a Varian Associates, Model 920 Aerograph with a thermal conductivity detector. A 10 foot 20% SE-30 on Chrom P column was used unless otherwise indicated.

Ultraviolet Spectra. Ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. The solvent used was 95% ethanol.

Mass Spectra. Mass spectra were determined by Mr. C. Weisenberger on a MS-9 mass spectrometer.

Anhydro-8-hydroxymercuri-1-naphthoic Acid (35).

1,8-Naphtholic anhydride (99 g, 0.50 mol) was suspended in aqueous sodium hydroxide (70 g, 1.75 mol in 3000 ml water) in a 12 liter flask and refluxed until all solid material had dissolved. Mercuric acetate (175 g, 0.55 mol) dissolved in water (500 ml) and glacial acetic acid (100 ml) was added to the sodium 1,8-naphthalate solution. After the mixture had been refluxed ~ 30 min, additional acetic acid (150 ml) was added to adjust the pH to 5. The resulting slurry was refluxed 48 hr, cooled to room temperature, and filtered. The tan solid was washed with distilled water and dried in vacuo at 80° for 18 hr. The yield of anhydro-8-hydroxymercuri-1-naphthoic acid was 180 g (97%).
**8-Bromo-1-naphthoic Acid (36).**

Anhydro-8-hydroxymercuri-1-naphthoic acid (186.0 g, 0.50 mol) was suspended in a solution of glacial acetic acid (760 ml) and water (120 ml) in a 3-necked round bottom flask, fitted with a condenser, an addition funnel, and a mechanical stirrer. The mixture was vigorously stirred and cooled to 0°. A solution of sodium bromide (340.0 g, 3.32 mol) in water (620 ml) and bromine (83.4 g, 28.6 ml, 0.52 mol) was placed in the addition funnel and added slowly to the contents of the flask while maintaining a reaction temperature of 0-5°. The resulting slurry was then heated to 100° and poured onto ice (~ 1500 g). The tan solid was washed with water and purified via solution as its sodium salt and reprecipitation with hydrochloric acid. The yield of 8-bromo-1-naphthoic acid was 79.8 g (64%), mp 172-173°, lit. 175-176°; ir(mull, cm⁻¹) 3350-2500 (broad, CO₂H), 1690 (acid C=O), 1580, 1200, 825, 769, 760 (aromatic); nmr(CDCl₃-DMSO-d₆, δ) 7.02-7.98 (m, 6H, aromatic) and 12.30 (broad s, 1H, CO₂H).

**8-Bromo-1-naphthoyl Chloride (37).**

A mixture of 8-bromo-1-naphthoic acid (200.8 g, 0.8 mol) and thionyl chloride (992.0 g, 600 ml, 8.4 mol)
was refluxed for 6 hr. The excess thionyl chloride was distilled off and the remaining traces removed under reduced pressure. The residue was recrystallized from hexane. The yield of 8-bromo-1-naphthoyl chloride was 180.0 g (86%), mp 66-68°, lit. 6 67-68°; ir(KBr, cm⁻¹) 1760(acyl C=O).

8-Bromo-1-naphthalenemethanol (38).

Lithium aluminum hydride (17.5 g, 0.46 mol) was suspended in anhydrous ethyl ether (500 ml) in a 5 3-necked round bottom flask, fitted with a condenser, an addition funnel, and a mechanical stirrer. A solution of 8-bromo-1-naphthoyl chloride (160.0 g, 0.61 mol) in ethyl ether (1500 ml) was added at a rate that maintained a moderate reflux. After addition was complete, the mixture was then refluxed 5 hr. The mixture was allowed to cool to room temperature and then hydrolyzed via addition of saturated aqueous sodium sulfate. The ethereal layer was decanted and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure leaving a pale yellow solid. The yield of 8-bromo-1-naphthalenemethanol was 130 g (88%); mp 84-86°(cyclohexane), lit. 8
86-87°; ir(KBr, cm⁻¹) 3500-3000(OH), 1610, 1500, 1070, 990, 890, 812, 762(aromatic); nmr(CDCl₃, δ) 2.57(broad s, 1H, CH₂OH), 5.30(broad s, 2H, CH₂OH), 6.86-7.80(m, 6H, aromatic).

8-Bromo-1-naphthaldehyde (39).

N-Chlorosuccinimide (80.0 g, 0.6 mol) was suspended in toluene (2000 ml) in a 5 3-necked round bottom flask fitted with an addition funnel, a mechanical stirrer, and a low temperature thermometer. The mixture was cooled to 0°, dimethyl sulfide (37.2 g, 45 ml, 0.6 mol) was added, and the resulting mixture was cooled to -25°. A solution of 8-bromo-1-naphthyl alcohol (70.8 g, 0.3 mol) in toluene (700 ml) was then added slowly to the cold N-chlorosuccinimide-dimethyl sulfide complex. The mixture was stirred for 2.5 hr at -25°. Triethylamine (45.0 g, 50 ml, 0.45 mol) was added and the mixture was allowed to warm to room temperature overnight and then filtered to remove the succinimide. The solution was concentrated (300 ml), poured into ether (1000 ml), and filtered. The ethereal solution was extracted with 1N hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride,
and dried over anhydrous magnesium sulfate. The solvents were removed under reduced pressure leaving a pale yellow solid. The yield of 8-bromo-1-naphthaldehyde was 63.0 g (85%); mp 86-88° (ethanol), lit. 89-90°; ir(KBr, cm⁻¹) 1660 (aldehyde C=O), 1600, 1550, 1490, 825, 792, 750 (aromatic); nmr(CDCl₃, δ) 7.12-8.02 (m, 6H, aromatic), 11.31 (s, 1H, CHO).

Rosenmund Reduction of 8-Bromo-1-naphthoyl Chloride (37).

8-Bromo-1-naphthoyl chloride (3.0 g, 11.1 mmol) was dissolved in dry xylene (25 ml) and placed in a 50 ml 3-necked round bottom flask fitted with a hydrogen inlet, a condenser with a gas outlet at the top, and a glass stopper. The hydrogen inlet extended below the surface of the solvent and the gas outlet exited at the bottom of an Erlenmeyer flask containing aqueous sodium hydroxide (0.420 g, 10.5 mmol in 250 ml water) and phenolphthalein (2 drops). Palladium on barium sulfate (5%, 30 mg) was added to the 8-bromo-1-naphthoyl chloride solution and hydrogen was slowly bubbled through the mixture heated to 80°. When the indicator solution turned clear, the hydrogen flow was stopped and the flask cooled to 0°. Ether was added, the solution filtered, and the solvent
removed under reduced pressure. Column chromatography of the residue on silica gel gave:

1. 1-Naphthaldehyde (41), 600 mg (34%), identical with an authentic sample.

2. 8-Bromo-1-naphthaldehyde (39), 610 mg (23%), identical with an authentic sample.

3. 8-Bromo-1-naphthoyl chloride (37), 1.05 g (35%), identical with an authentic sample.

Oxidation of 8-Bromo-1-naphthalenemethanol (38) with Sodium Hypochlorite.10

8-Bromo-1-naphthalenemethanol (9.5 g, 40 mmol) was dissolved in ethyl acetate (200 ml) and chlorox (200 ml of a 5.25% aqueous solution of sodium hypochlorite) was added to form the two phase system. Benzyltriethylammonium chloride (1 g) was added as a phase transfer catalyst and the mixture stirred vigorously for 30 hr. The stirring was stopped and the organic layer was separated; pentane (200 ml) was added, and the organic layer was washed with three 200 ml portions of water. After drying the extract with magnesium sulfate, the solvent was removed under reduced pressure to leave
8-bromo-1-naphthaldehyde (7.6 g, 81%) identical to an authentic sample by ir, nmr, and tlc.

8-Bromo-1-naphthaldehyde p-Tosylhydrazone (40).

8-Bromo-1-naphthaldehyde (55.0 g, 0.224 mol) was dissolved in ethanol (100 ml) and added quickly with stirring to a hot solution of p-tosylhydrazide in ethanol (300 ml). After the mixture had cooled to room temperature, the white solid that formed was suction-filtered and then recrystallized from ethanol. The yield of 8-bromo-1-naphthaldehyde p-tosylhydrazone was 72.0 g (80%), mp 192-194°, lit. 193-195°; ir (KBr, cm\(^{-1}\)) 3200 (NH), 1600, 1490, 1450, 940, 895, 812, 754 (aromatic), 1440, 1150 (SO\(_2\)).

1-Bromo-1H-cyclobuta[de]naphthalene (4).

Sodium hydride (4.60 g of 50% in mineral oil, 0.1 mol) was washed with pentane, slurried in dry dichloromethane (700 ml), and cooled to 0°. 8-Bromo-1-naphthaldehyde p-tosylhydrazone (40.2 g, 0.1 mol) was added very slowly with stirring to the sodium hydride slurry. The stirring was continued for 15 min after hydrogen evolution ceased. The resulting yellow solution was evaporated to dryness. The sodium 8-bromo-1-naphthaldehyde
p-tosylhydrazonate was slurried in anhydrous ethyl ether (2300 ml) and irradiated for 16 hr with a 450W Hanovia 679A36 high pressure mercury arc lamp under nitrogen. The mixture was filtered and the solvent removed under reduced pressure. The residue was absorbed onto silica gel (30 g) and column chromatography using hexane as eluent gave:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (4), 9.3 g (43%), mp 100-103°, lit. 8 102-104°; ir (KBr, cm\(^{-1}\)) 1600, 1460, 1145, 1005, 980, 820, 785, 775, 680 (aromatic); nmr (CDCl\(_3\), \(\delta\)) 6.76 (s, 1H, bridge), 7.18 (d of d, 2H, \(J = 5\) and 2 Hz, ortho); 7.30-7.68 (m, 4H, meta and para).

2) Trans-bis(8-bromo-1-naphthyl)ethylene, 4.3 g (10.0%), mp 199-202, lit. 3 203-204°; nmr(CDCl\(_3\), \(\delta\)) 6.0-8.0 (m).

1H-Cyclobuta[de]naphthalene (1).

1-Bromo-1H-cyclobuta[de]naphthalene (4.4 g, 20 mmol) was dissolved in anhydrous ethyl ether (100 ml). Red-al (20 ml, a 70% solution of sodium bis(2-methoxyethoxy) aluminum hydride in benzene) was added to the mixture at a rate that maintained a reflux and the solution was then
refluxed an additional 12 hr. The mixture was cooled to room temperature and quenched with ethyl acetate followed by water. The organic layer was separated, extracted with water, dried over magnesium sulfate, and the solvent removed under reduced pressure to leave a colorless oil. Vacuum distillation of the oil produced pure 1H-cyclobuta-[de]naphthalene; 2.10 g (75%), bp 84-90° (0.50 mm). The product by its nmr, ir, and mass spect was identical to that prepared by Bailey.

Nitration of 1H-Cyclobuta[de]naphthalene (1).

1H-Cyclobuta[de]naphthalene (0.140 g, 1.0 mmol) was dissolved in glacial acetic acid (2 ml) and cooled to 0°. Nitric acid (0.30 g of 70%, 3.0 mmol) was mixed with concentrated sulfuric acid (0.5 ml) and added to the acetic acid solution over a 3 min period, stirred an additional 3 min, and poured onto ice. The mixture was neutralized with sodium bicarbonate and extracted with ether. The ethereal layer was dried over magnesium sulfate and the solvent removed under reduced pressure. Column chromatography of the residue on silica gel gave:

1) 4-Nitro-1H-cyclobuta[de]naphthalene (42), 75 mg (41%), as a yellow solid, mp 124-125°; ir(KBr,
98

\[ \text{cm}^{-1} \) 1505, 1300\((\text{NO}_2)\), 1600, 1575, 1460, 1435, 1405, 1180, 890, 855, 780\((\text{aromatic})\); \text{nmr}(\text{CDCl}_3, \delta) 4.73(s, 2H, \text{CH}_2), 7.16(d, 1H, J = 6Hz, aromatic on C_7), 7.21(d, 1H, J = 7Hz, aromatic on C_2), 7.65(d of d, 1H, J = 9 and 6Hz, aromatic on C_6), 8.19(d, 1H, J = 9Hz, aromatic on C_5), 8.48(d, 1H, J = 7Hz, aromatic on C_3); \text{uv}(\lambda, \epsilon) 346\text{ nm}(5450), 254(10,600), 213(37,200); \text{exact mass: calcd.} 185.04766; \text{found 185.04799.}

\text{Anal. Calcd. for } C_{11}H_7\text{NO}_2: C, 71.35; H, 3.78.
\text{Found: } C, 70.97; H, 3.99.

2) 4,5-Dinitro-1H-cyclobuta[de]naphthalene (43), 55 mg (24\%) as a pale yellow solid, mp 166-168\(^\circ\); \text{ir}(\text{KBr, cm}^{-1}) 1510, 1315\((\text{NO}_2)\), 1610, 1575, 1350, 910, 845, 816, 755\((\text{aromatic})\); \text{nmr}(\text{CDCl}_3, \delta) 4.81 (2H, \text{CH}_2), 7.39(d, 2H, J = 7Hz, \text{ortho}), 8.85 (d, 2H, J = 7Hz, \text{meta}); \text{C}^{13}\text{nmr}(\text{CDCl}_3, \delta) 45.6(1C, C_1), 109.4(1C, C_9), 119.8(2C, C_2,7), 131.2(2C, C_3,6), 142.1(1C, C_8), 145.5(2C, C_4,5), 146.2(2C, C_{1a},7a); \text{uv}(\lambda, \epsilon) 329\text{ nm}(6615), 238(24,500), 201(37,400); \text{exact mass: calcd.} 230.03273; \text{found, 230.03223.}

\text{Anal. Calcd. for } C_{11}H_6\text{N}_2\text{O}_4: C, 57.40; H, 2.62.
\text{Found: } C, 56.95; H, 2.50.
Nitration of 1-H-Cyclobuta[de]naphthalene (1) with Acetyl Nitrate.

Acetyl nitrate (7.5 mmol) was prepared by adding 70% nitric acid (700 mg, 7.5 mmol) slowly at 0° to acetic anhydride (5 ml). This mixture was added dropwise to a solution of 1H-cyclobuta[de]naphthalene (1.0 g, 7.1 mmol) in acetic anhydride (20 ml) at 0-5°. The mixture was stirred for an additional hour and allowed to warm to room temperature. Ether (300 ml) and 20% potassium hydroxide (200 ml) was added and the mixture was stirred for 2 hr to hydrolyze the acetic anhydride. The ethereal layer was separated, dried over magnesium sulfate, and the solvent removed under reduced pressure leaving 4-nitro-1H-cyclobuta[de]naphthalene (42, 1.12 g, 85%), identical with an authentic sample.

Nitration of 4-Nitro-1H-cyclobuta[de]naphthalene (42).

A mixture of concentrated sulfuric acid (10 ml) and nitric acid (70%, 16 ml) at room temperature was added to 4-nitro-1H-cyclobuta[de]naphthalene (125 mg, 0.66 mmol) in acetic acid (10 ml). This mixture was stirred 30 min, poured into water, neutralized with sodium bicarbonate, and extracted with ether. The ethereal layer was dried
with magnesium sulfate, the solvent removed under reduced pressure, and the residue passed through a layer of silica gel with benzene. The solvent was removed leaving 4,5-dinitro-1H-cyclobuta[de]naphthalene (43, 0.140 g, 89%), identical with an authentic sample.

Nitration of 1-Bromo-1H-cyclobuta[de]naphthalene (4).

1-Bromo-1H-cyclobuta[de]naphthalene (0.62 g, 2.8 mmoles) was dissolved in acetic anhydride (3 ml). To this was added a solution of acetic anhydride (5 ml) in nitric acid (70%, 0.44 ml) at 0°. This mixture was then stirred 30 min, poured into water, neutralized with sodium bicarbonate, and extracted with ether. The ethereal layer was dried and the solvent removed under reduced pressure to yield 1-bromo-4-nitro-1H-cyclobuta[de]naphthalene (44, 0.50, 67%), mp 115-117°; ir (KBr, cm⁻¹) 1510, 1310 (NO₂), 1430, 1340, 1150, 893, 778, 728 (aromatic); nmr (CDCl₃, δ) 6.73 (s, 1H, bridge), 7.27 (d, 1H, J = 8 Hz, aromatic on C₇), 7.35 (d, 1H, J = 7 Hz, aromatic on C₂), 7.78 (d of d, 1H, J = 8 and 8 Hz, aromatic on C₆), 8.28 (d, 1H, J = 8 Hz, aromatic on C₅), 8.50 (d, 1H, J = 7, aromatic on C₃); uv (λ, ε) 347 nm (4,800), 253 (9,300), 224 (shoulder, 16,500), 215 (21,000); exact mass: calcd. 262.95822; found, 262.95858.
An analytical sample was prepared by two sublimations at 80-90° (0.1 mm) and recrystallization from hexane.

Anal. Calcd. for C_{11}H_{6}BrNO_2: C, 50.03; H, 2.29.

Found: C, 49.99; H, 2.40.

Acetylation of 1H-Cyclobuta[de]naphthalene (1).

A mixture of 1H-cyclobuta[de]naphthalene (140 mg, 1.0 mmol) and acetyl chloride (78 mg, 1.0 mmol) was dissolved in dichloromethane (6 ml). To this was added aluminum chloride (130 mg, 1 mmol) slowly over 1 hr and then the reaction mixture was stirred for 8 hr. The resulting dark solution was poured into water and extracted with ether; the ethereal layer was dried with magnesium sulfate, and the solvent removed under reduced pressure. The residue was passed through a short column of silica gel with benzene. The benzene was removed to yield 4-acetyl-1H-cyclobuta[de]naphthalene (__, 140 mg, 61%). An analytical sample was prepared by sublimation at 130° (0.1 mm), mp 39-42°; ir(KBr, cm^{-1}) 1665(C=O), 1580, 1460, 1345, 1305, 1260, 952, 830, 783(aromatic); nmr(CDCl_3, δ) 2.51(s, 3H, CH_3), 4.53(s, 2H, CH_2), 6.89(d, 1H, J = 6Hz, H on C_7), 6.99(d, 1H, J = 4Hz, H on C_2), 7.39(d of d, 1H, J = 6 and 7Hz, H on C_6), 7.85(d, 1H, J = 7Hz, H on C_5), 8.19(d, 1H, J = 4Hz, H on C_3); uv(λ, ε) 324 nm (5310), 313(5600),
227(23,400), 208(24,100), 198(26,100); exact mass: calcd. for \( \text{C}_{13}\text{H}_{10}\text{O} \), 182.07315; found, 182.07345.

**Anal.** Calcd. for \( \text{C}_{13}\text{H}_{10}\text{O} \): C, 85.69; H, 5.53.

**Found:** C, 85.43; H, 5.90.

4-Acetyl-1\(H\)-cyclobuta[de]naphthalene 2,4-Dinitrophenyl-hydrazone.

4-Acetyl-1\(H\)-cyclobuta[de]naphthalene (100 mg, 0.55 mmol) and 2,4-dinitrophenylhydrazene (105 mg, 0.575) were dissolved in absolute ethanol (20 ml) and concentrated hydrochloric acid (1 drop) was added. The reaction mixture was stirred 2 hr at room temperature. The orange precipitate that formed was collected and washed with cold ethanol to yield 4-acetyl-1\(H\)-cyclobuta[de]naphthalene 2,4-dinitrophenylhydrazone (110 mg, 56%). Recrystallization from benzene gave an analytical sample, mp 251-252\(^\circ\); ir(KBr, cm\(^{-1}\)) 1610, 1580, 1505, 1320, 1290, 1250, 1120, 1080, 830, 783; exact mass: calcd. for \( \text{C}_{19}\text{H}_{14}\text{N}_{4}\text{O}_{4} \), 362.10148; found, 362.10186.

**Anal.** Calcd. for \( \text{C}_{19}\text{H}_{14}\text{N}_{4}\text{O}_{4} \): C, 62.98; H, 3.89.

**Found:** C, 63.22; H, 4.01.
4-(1-Phenylacetyl)-1H-cyclobuta[de]naphthalene (46).

Phenylacetyl chloride (250 mg, 1.6 mmol) and 1H-cyclobuta[de]naphthalene (200 mg, 1.5 mmol) were dissolved in dichloromethane. Aluminum chloride (220 mg, 1.6 mmol) was added slowly over 1 hr to this solution and, after the addition was complete, the reaction mixture was stirred for 8 hr. The dark solution was then poured into water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and the solvent removed under reduced pressure. The residue was passed through a short column of silica gel with benzene and the solvent removed to yield 4-(1-phenylacetyl)-1H-cyclobuta[de]naphthalene (46, 320 mg, 87%). An analytical sample was prepared by recrystallization from hexane and sublimation at 80-100° (0.1 mm), mp 91.5-93.5°; ir(KBr, cm⁻¹) 1660(C=O), 1460, 1300, 1230, 1130, 975, 835, 788, 705; nmr(CDCl₃, δ) 4.23(s, 2H, CH₂ next to C=O), 4.57(s, 2H, CH₂ bridge), 7.18(broad s, 5H, phenyl), 6.98(d, 1H, J = 7Hz, H on C₇), 7.03(d, 1H, J = 7Hz, H on C₂), 7.47(d of d, 1H, J = 7Hz and 7Hz, H on C₆), 8.06(d, 1H, J = 7Hz, H on C₅), 8.29(d, 1H, J = 7Hz, H on C₃); uv(λ, ε) 318 nm(7,800), 242(22,750),
227(29,500), 211(32,000); exact mass: calcd. for $C_{19}H_{14}O$
258.10445, found 258.10499.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46.
Found: C, 88.04; H, 5.55.

**Diacetylation of $\text{1H-Cyclobuta[de]naphthalene (1)}$.**

$\text{1H-Cyclobuta[de]naphthalene (140 mg, 1 mmol)}$ and acetyl chloride (200 mg, 2.5 mmol) were dissolved in 1,2-dichloroethane (10 ml) and aluminum chloride (320 mg, 2.5 mmol) was added slowly at room temperature and the mixture refluxed for 36 hr. The dark solution was then poured into water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and the solvent removed under reduced pressure. The residue was passed through a short column of silica gel with benzene and the solvent removed to yield a single product, 4-acetyl-$\text{1H-Cyclobuta[de]naphthalene (45, 125 mg, 69%)},$ identical with an authentic sample.

**Reaction of $\text{1H-Cyclobuta[de]naphthalene (1)}$ with Bromine and Iron.**

$\text{1H-Cyclobuta[de]naphthalene (350 mg, 2.5 mmol)}$ was dissolved in carbon tetrachloride (5 ml) and powdered iron
(20 mg) was added. To this mixture a solution of bromine (400 mg, 2.5 mmole) in carbon tetrachloride (10 ml) was added slowly at 0° in the dark. After the addition was complete, the mixture was stirred 4 hr at room temperature, then hexane (100 ml) was added, and the mixture was filtered through several inches of silica gel. The solvent was removed under reduced pressure to leave 4-bromo-1H-cyclobuta[de]naphthalene (47) as a pale yellow oil (520 mg, 94%). The oil was distilled (105-120°; 0.1 mm) to yield pure bromide; mp 21-23°; ir(KBr, cm⁻¹) 3090, 2960, 1460, 1430, 1405, 1315, 1180, 1000, 820, 775, 750; nmr(CDCl₃, δ) 4.50 (s, 2H, CH₂), 6.7-7.55 (m, 5H, aromatic); uv(λ, ε) 320 nm (430), 316 (602), 300 (3150), 289 (5280), 281 (5125), 227 (55, 330); exact mass: calcd. for C₁₁H₇Br 217.9732; found, 217.9737.

Anal. Calcd. for C₁₁H₇Br: C, 60.30; H, 3.22.
Found: C, 59.78; H, 3.44.

4-Bromo-1H-cyclobuta[de]naphthalene Picrate.

A solution of picric acid (110 mg, 0.48 mmol) in hot ethanol (2 ml) was mixed with a solution of 4-bromo-1H-cyclobuta[de]naphthalene (100 mg, 0.46 mmol) in hot ethanol (2 ml). The mixture was allowed to cool to room temperature and the yellow crystals that formed were collected
and washed with cold ethanol. Recrystallization from ethanol gave an analytical sample of 4-bromo-1H-cyclobuta[de]naphthalene picrate, mp 107-108°.

**Anal.** Calcd. for C_{17}H_{10}BrN_{3}O_{7}: C, 45.56; H, 2.25. Found: C, 45.59; H, 2.33.

**Bromination of 4-Bromo-1H-cyclobuta[de]naphthalene (47).**

Bromine (160 mg, 1 mmol) in carbon tetrachloride (10 ml) was added slowly at 0° to a mixture of 4-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol), carbon tetrachloride (5 ml), and powdered iron (20 mg). After the addition was complete the reaction mixture was stirred an hour at room temperature, diluted with hexane, filtered through a pad of silica gel, and the solvent removed under reduced pressure. The white crystalline residue (265 mg, 89%) was identified as 4,5-dibromo-1H-cyclobuta[de]naphthalene (48), mp 142-144°; ir(KBr, cm^{-1}) 3040, 2990, 1470, 1425, 1300, 1120, 1040, 860, 830; nmr (CDCl_{3}, δ) 4.39(s, 2H, CH_{2}), 6.82(d, 2H, J = 7Hz, ortho), 7.59(d, 2H, J = 7Hz, meta); C^{13} nmr (CDCl_{3}, δ) 44.2(1C, C_{1}), 113.5(2C, C_{4,5}), 119.8(2C, C_{2,7}), 123.5(1C, C_{9}), 136.3(2C, C_{3,6}), 140.4(2C, C_{1a,7a}), 146.2(1C, C_{8}); uv(λ, ε) 328 nm(1,400), 317(4,000), 303(6,450), 292(5,650),
232(32,000); exact mass: calcd. for $\text{C}_{11}\text{H}_6\text{Br}_2$ 395.8837; found, 395.8841.

**Anal.** Calcd. for $\text{C}_{11}\text{H}_6\text{Br}_2$: C, 44.34; H, 2.03.

Found: C, 44.51; H, 2.19.

**Comparative Rates of Electrophilic Substitution of**

1H-Cyclobuta[de]naphthalene (1) versus Naphthalene (52),  
Acenaphthene (49), and 2,3-Dihydro-1H-phenalen (51).

**Comments on the General Procedures.**

Standard samples of 1 to 1 mixtures of 1H-cyclobuta-[de]naphthalene with naphthalene, 1H-cyclobuta[de]-naphthalene with acenaphthene, and 1H-cyclobuta[de]-naphthalene with 2,3-dihydro-1H-phenalen were prepared by mixing 1H-cyclobuta[de]naphthalene (1.4 g, 10 mmol) with 10 mmol of each of the other hydrocarbons. Each reaction—nitration, acetylation, and bromination—was carried out twice on each sample mixture using 10 to 10 to 1 mole ratios of hydrocarbon to hydrocarbon to reactant. The molar ratio of hydrocarbons was always 1 to 1 within experimental error. This was checked by nmr and gc (correcting for relative responses) before and after each reaction, making corrective adjustments on the standard samples when necessary.
**General Procedures**

**Nitration.** The standard sample of hydrocarbons (10 mmol each) was dissolved in acetic anhydride (50 ml) and stirred vigorously at 0°. To this was added slowly acetyl nitrate (prepared from 10 ml of acetic anhydride and 90 mg of 70% nitric acid (1 mmol). The solution was stirred an additional hour, poured into aqueous sodium hydroxide, stirred 15 min, and extracted with ether. The ethereal layer was dried with magnesium sulfate, the solvent removed under reduced pressure, and the residue passed through a short column of silica gel with hexane to quickly separate the unreacted hydrocarbon from the nitro fractions. The nitro fraction was analyzed by nmr. The hydrocarbon mixture was calibrated, corrected, and reused.

**Acetylations.** The standard sample of hydrocarbons (10 mmol each) was dissolved in methylene chloride (50 ml) along with acetyl chloride (70 mg, 1 mmol). The solution was stirred vigorously at room temperature while aluminum chloride (132 mg, 1 mmol) was added slowly. The stirring was continued for 10 hr, then the solution was poured into water and extracted with methylene chloride. The
organic layer was dried, the solvent removed under reduced pressure, and the residue chromatographed quickly on silica gel with hexane to separate the hydrocarbon fraction from the ketone fraction. The ketone fraction was analyzed by nmr and the hydrocarbon fraction reused as described before.

**Bromination.** The standard sample of hydrocarbons (10 mmol each) was dissolved in carbon tetrachloride (40 ml). Iron fillings (15 mg) were placed in the flask and bromine (180 mg, 1 mmol) dissolved in carbon tetrachloride (10 ml) was added slowly with vigorous stirring in the dark. The stirring was continued for 6 hr, the solution filtered, and then concentrated in vacuo to about 10 ml. The products were then analyzed by gas chromatography.

**Results.** The product ratios for the runs were determined, averaged, and are shown in Table 1. The ratios for naphthalene (52) were adjusted for the fact that naphthalene (52) has 4 active positions for electrophilic substitution while 1H-cyclobuta[de]naphthalene (1) has only 2. The products of each reaction were isolated, compared with authentic samples, and the yields determined. The yields for all nitrations were approximately 85%; for
Friedel-Crafts acetylations 75%; and for brominations 90%. For all nitrations and brominations only the "para" substituted compounds were isolable. For the Friedel-Crafts reactions the "para" isomer was major, but about 10-15% "ortho" isomer was detected (following synthesis of authentic samples gives more details).

**Authentic Samples.**

1-Nitronaphthalene was purchased commercially and was identical to that obtained in the rate studies by tlc, nmr, and mp: 54-56° (lit. 36 55-56°).

1-Acetylnaphthalene was prepared by dissolving naphthalene (128 mg, 1 mmol) and acetyl chloride (78 mg, 1 mmol) in methylene chloride (15 ml) and then adding aluminum chloride (132 mg, 1 mmol). The solution was stirred 6 hr at room temperature, poured into water, extracted with methylene chloride, and the organic layer dried with magnesium sulfate. Removal of the solvent left a ketone mixture which was shown by ir to be 1-acetyl-naphthalene and 2-acetylnaphthalene in a ratio of about 6 to 1. The important ir frequencies are 919, 860, 799, 777, 750 cm⁻¹ and 903, 872, 835, 775, 755, respectively.
1-Bromonaphthalene, purchased commercially, was shown by nmr, ir, and gc to be identical with that from the rate studies.

5-Nitroacenaphthalene was prepared by slowly adding acetyl nitrate (prepared from 100 mg of 70% nitric acid and 5 ml of acetic anhydride) to acenaphthalene (154 mg, 1 mmol) in acetic anhydride (10 ml) at 5°. The solution was stirred for 1 hr at room temperature, poured into 10% aqueous sodium hydroxide, stirred 30 min, and extracted with ether. The ethereal layer was dried with magnesium sulfate and removal of the solvent under reduced pressure left 5-nitroacenaphthene as the only detectable product. This was proven by comparison to literature ir frequencies of 900 cm\(^{-1}\), 846, 830, 815, 800, 772, 710. The melting point was 107-109° (lit. 108-110°).

5-Acetylacenaphthene was prepared from acenaphthene (1 mmol) by a procedure similar to that used for naphthalene. The ketone product contained both 5-acetylacenaphthene and 3-acetylacenaphthene in a ratio of 8 to 1. The identification was established by comparison to literature ir frequencies of 890 cm\(^{-1}\), 845, 835, 775, and 750 for the 3-isomer and 905, 842, and 775 for the 5-isomer.
5-Bromoacenaphthlene was prepared by dissolving acenaphthene (154 mg, 1 mmol) in carbon tetrachloride (20 ml) and adding powdered iron (20 mg). Bromine (160 mg, 1 mmol) dissolved in carbon tetrachloride was then added slowly at 0° in the dark to the acenaphthene flask. The solution was then stirred 2 hr at room temperature, filtered, and the solvent removed under reduced pressure. The residue was identified as 5-bromoacenaphthene by its mp 48-51° (lit. 52°) and by comparison to literature ir frequencies of 885 cm⁻¹, 846, 835, 815, 770, 740, respectively.

6-Nitro-1H-2,3-dihydrophenalene was prepared by a procedure similar to that for 5-nitroacenaphthene except that 1H-2,3-dihydro-phenalene (1 mmol) was used. The yield of 6-nitro-1H-2,3-dihydrophenalene was 182 mg (86%), mp 85-87°; ir(KBr, cm⁻¹) 3050, 1580, 1425, 805, 765 (aromatic), 1495, 1310(NO₂), 2960(CH₂); nmr(CDCl₃, δ) 2.01(broad quintet, 2H, H on C₂), 3.03(broad t, 4H, H on C₁ and C₃), 6.95-8.4(m, 5H, aromatic); exact mass: calcd. for C₁₃H₁₁NO₂, 213.0790; found 213.0793.

6-Acetyl-1H-2,3-dihydrophenalene was prepared by a procedure similar to that for 1-acetylnaphthalene except that 1H-2,3-dihydrophenalene (1 mmol) was used.

6-Bromo-1H-2,3-dihydrophenalene was prepared by a procedure similar to that for 5-bromoacenaphthene except that 1H-2,3-dihydrophenalene (1 mmol) was used. The product had a mp of 24-25° (lit. 24-25°).

Synthesis of 1H-2,3-dihydrophenalene (50).

1H-Phenalene-1-one hydrazone (8.7 g, 50 mmol) was slurried in toluene (200 ml) and potassium t-butoxide (16.4 g, 200 mmol) was added all at one. The mixture was refluxed 2 hr until nitrogen evolution stopped. Dilute hydrochloric acid was then added and the solution was extracted with ether. The ethereal layer was dried with magnesium sulfate, and the solvent was removed under reduced pressure. The residue was passed through a short column of silica gel with hexane to yield 1H-phenalene (1.15 g, 14%), identified by its mp 84-86° (lit. 85-86°) and nmr (CDCl₃, 6) 3.91 (broad s, 2H, CH₂), 5.88 (d of t, 1H, J = 2Hz and 9Hz, H on C₂), 6.49 (d of t, 1H, J = 2Hz and 6Hz, H on C₃), 6.8-7.8 (m, 6H, aromatic) which match literature values.
1H-Phenalene (1.15 g, 7 mmol) was dissolved in methanol (40 ml) and hydrogenated in a Parr apparatus at 2 atm for 3 hr using 10% palladium on carbon (10 mg) as catalyst. The mixture was then filtered and the solvent removed under reduced pressure to yield 1H-2,3-dihydrophenalene (50, 1.05 g, 89%). The nmr of 50 was identical to that in the literature: 42 1.97 (broad q, 2H, H on C2), 3.01 (broad t, 4H, benzylic H), and 6.9-7.6 (m, 6H, aromatic).

Hydrogenation of 4-Nitro-1H-cyclobuta[de]naphthalene (42).

4-Nitro-1H-cyclobuta[de]naphthalene (185 mg, 1 mmol) was dissolved in methanol (50 ml) and palladium on carbon (5%, 10 mg) was added. The mixture was hydrogenated in a Parr apparatus at 1.5 atmospheres for 30 min, and then removed from the apparatus. Ether (100 ml) was added, the mixture was filtered through a double layer of filter paper, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel eluting with hexane-benzene to yield two products:

1) 4-Nitro-1H-cyclobuta[de]naphthalene (42), 66 mg (36%), identical with an authentic sample.
2) 4-Amino-1H-cyclobuta[de]naphthalene (56), 86 mg (55%), bp 130-135° (0.15 mm); ir (KBr, cm⁻¹) 3450, 3360 (NH₂), 3040, 2960, 2920, 1675, 1610, 1490, 1450, 1325, 1275, 820, 780, 750; nmr (CDCl₃, δ) 4.64 (s, 2H, CH₂), 4.87 (broad s, 2H, NH₂), 6.53 - 7.60 (m, 5H, aromatic); exact mass: calcd. for 155.07349; found, 155.07358.

1-(1H-Cyclobuta[de]naphthalen-4-yl)-3-phenyl-2-thiourea.

A solution of 4-amino-1H-cyclobuta[de]naphthalene (155 mg, 1 mmol) and phenyl isothiocyanate (135 mg, 1 mmol) in methanol (6 ml) was stirred 2 hr at room temperature. The solid that formed was recrystallized from ethanol and identified as 1-(1H-cyclobuta[de]naphthalen-4-yl)-3-phenyl-2-thiourea (180 mg, 62%), mp 184-187°; exact mass: calcd. for C₁₈H₁₄N₂S, 290.0879; found, 290.0885.

Anal. Calcd. for C₁₈H₁₄N₂S: C, 74.45; H, 4.86; N, 9.65. Found: C, 74.65; H, 4.50; N, 9.35.

Reduction of 4-Nitro-1H-cyclobuta[de]naphthalene (42) with Tin and Hydrochloric Acid.

Powdered tin (600 mg) was added to 4-nitro-1H-cyclobuta[de]naphthalene (185 mg, 1 mmol), cooled to 0°,
and concentrated hydrochloric acid (3 ml) was added. The mixture was stirred 20 min, ethanol (10 ml) was added, the solution was refluxed 1.5 hr, and then stirred overnight at room temperature. The dark solution was worked up by pouring into ether, neutralizing with sodium bicarbonate, drying with magnesium sulfate, and chromatography on silica gel eluting with benzene. Thus 4-amino-1H-cyclobuta[de]naphthalene (24 mg, 13%) was obtained identical with an authentic sample. The remainder of the material was not identified but appeared to be high molecular weight material.

Reduction of 4-Nitro-1H-cyclobuta[de]naphthalene (42)

4-Nitro-1H-cyclobuta[de]naphthalene (600 mg, 3.2 mmol) was placed in a 250 ml 3-necked round bottom flask fitted with a nitrogen inlet, a glass stopper, and a condenser with a nitrogen outlet at the top. To this was added diethyl ether (125 ml), ethanol (40 ml), and water (25 ml) to effect solution. The reduction was commenced by adding activated amalgamated aluminum strips (1.5 g) over a period of 1 hr, which caused noticeable hydrogen evolution, and stirring the solution overnight. The
activated strips were prepared by cutting aluminum foil into 1 by 3 cm strips and dipping them successively (15 sec each) into aqueous sodium hydroxide (10%), water, ethanol, ether, aqueous mercuric chloride (2%), water, ethanol, and ether and then quickly inserting the strips into the reaction flask. The mixture was worked up by filtering through celite, washing the celite with ether, and concentrating the solvent to 100 ml. After water had been added, the product was extracted with chloroform, the organic layer dried, and the solvent removed under reduced pressure to yield 4-amino-1H-cyclobuta[de]-naphthalene (56, 470 mg, 77%), identical to an authentic sample.

Alternate Synthesis of 4-Bromo-1H-cyclobuta[de]naphthalene (47).

4-Amino-1H-cyclobuta[de]naphthalene (250 mg, 1.6 mmol) was cooled to 0° and hydrobromic acid (48%, 1 ml) was added. Nitrous acid, prepared by adding hydrobromic acid (48%, 2 ml) slowly to a cold solution of sodium nitrite (140 mg, 2 mmol) in water (5 ml), was added dropwise to the cold reaction mixture then was stirred 15 min. Copper (I) bromide (0.5 g) was added and the
mixture was refluxed 30 min, poured into water, neutralized with sodium bicarbonate and extracted with ether. The ethereal layer was dried with magnesium sulfate, the solvent removed under reduced pressure, and the residue chromatographed on silica gel eluting with hexane. 4-Bromo-1H-cyclobuta[de]naphthalene (47, 38 mg, 11%) was obtained identical spectrally to an authentic sample. The remainder of the material remained unidentified.

Stability of 1H-Cyclobuta[de]naphthalene (1) to Tin and Hydrochloric Acid.

A mixture of 1H-cyclobuta[de]naphthalene (140 mg, 1 mmol) and powdered tin (200 mg), was cooled to 0° and concentrated hydrochloric acid (2 ml) was added. The mixture was stirred vigorously while warming to room temperature, then ethanol (5 ml) was added and the mixture was refluxed for 2 hr. The solution was poured into water, neutralized with sodium bicarbonate, and extracted with ether. The ethereal layer was dried with magnesium sulfate, and the solvent removed under reduced pressure to yield 1H-cyclobuta[de]naphthalene (1, 122 mg, 87%) identical with an authentic sample.
Stability of 1H-Cyclobuta[de]naphthalene (1) to Hydrobromic Acid.

1H-Cyclobuta[de]naphthalene (140 mg, 1 mmol) was cooled to 0° and hydrobromic acid (48%, 3 ml) was added. After stirring the mixture 1 hr ethanol (5 ml) was added and the mixture was refluxed 12 hr. The solution was poured into water, neutralized with sodium bicarbonate, and extracted with ether. After the ethereal layer had been dried with magnesium sulfate the solvent was removed under reduced pressure to yield 1H-cyclobuta[de]naphthalene (1, 116 mg, 83%) identical to an authentic sample.

Grignard Reaction of 4-Bromo-1H-cyclobuta[de]naphthalene (47).

Magnesium turnings (30 mg, 1.3 mmol) were added to 4-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) in dry tetrahydrofuran (20 ml) and the mixture refluxed 6 hr under nitrogen. The light green solution was cooled to -20° at which time acetyl chloride (1 ml) was added via syringe. Then the mixture was allowed to warm up to room temperature and finally refluxed 2 hr. Removal of the volatiles under reduced pressure left a tan semi-solid
residue whose tlc revealed a large number of difficultly separable compounds. The products were not identified further.

**Attempted Reaction of 4-Lithio-1H-cyclobuta[de]naphthalene with Acetaldehyde.**

4-Bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) in dry tetrahydrofuran (20 ml) was cooled to -78°, and n-butyllithium (1.2 eq) was added under nitrogen via syringe. After stirring the mixture 15 min, acetaldehyde (2 ml) was added and the solution warmed to room temperature in 3 hr. Reduced pressure removed the volatiles, but again tlc showed a large number of products present -- none of which were major. No further identification was attempted.

**Deuteration Studies on 4-Lithio-1H-cyclobuta[de]naphthalene.**

Various samples of 4-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) were dissolved in dry tetrahydrofuran (20 ml) and n-butyllithium (0.55 mmol) was added at -78° under nitrogen. Deuterium oxide (2 ml) was added to these samples at selected time intervals. After the mixtures had warmed to room temperature, the organic layer was
separated, dried with magnesium sulfate, and the solvent removed under reduced pressure. The products, deuterated samples of 1H-cyclobuta[de]naphthalene (1), were analyzed by nmr and mass spectroscopy (see Table 2 for a summary of results).

**Addition of Hydrogen Bromide to 1-Ethylidene-1H-cyclobuta[de]naphthalene (23).**

Gaseous hydrogen bromide was passed through a drying tube containing copper turnings and collected in a trap (-78°) containing 1-ethylidene-1H-cyclobuta[de]naphthalene (166 mg, 1 mmol) in methylene chloride (5 ml). The collection was continued until about 2 ml of hydrogen bromide had been condensed. The mixture was stirred at -78° for 2 hr and warmed to room temperature in 6 hr as the excess hydrogen bromide evaporated. The solvent was removed under reduced pressure to yield 1-bromo-1-ethyl-1H-cyclobuta[de]naphthalene (63, 220 mg, 89%), as the only identifiable product; ir(thin film, cm⁻¹) 3010, 2910, 1440, 1360, 1250, 1160, 1070, 880, 775; nmr(CDCl₃, δ) 1.23(t, 3H, J = 6Hz, CH₃), 2.50(q, 2H, J = 6Hz, CH₂−).
7.10 (d of d, 2H, $J = 2$Hz and 6Hz, ortho), 7.35-7.65 (m, 4H, meta and para); exact mass: calcd. for $C_{13}H_{11}Br$
246.00446; found, 246.00494.

Addition of Hydrogen Bromide to 1-Isopropylidene-1H-
cyclobuta[de]naphthalene (24).

Hydrogen bromide was added to 1-isopropylidene-1H-
cyclobuta[de]naphthalene (180 mg, 1 mmol) using the same
procedure and workup as that for 1-ethylidene-1H-
cyclobuta[de]naphthalene. The product mixture contained
two inseparable compounds in the ratio of 9 to 1. The
yield was 230 mg (88%).

1) 1-Bromo-1-isopropyl-1H-cyclobuta[de]naphthalene
(64, major); nmr(CDCl$_3$, $\delta$) 1.27 (d, 6H, $J = 6$Hz,
CH$_3$), 2.3 (sextet, 1H, $J = 6$Hz, $-\text{CH(CH}_3)\text{}_2$, 7.0-7.7 (m, 6H, aromatic).

2) 1-(1-bromoisopropyl)-1H-cyclobuta[de]naphthalene
(65, minor); nmr(CDCl$_3$, $\delta$) 1.83 (s, 6H, CH$_3$), 5.69
(s, 1H, bridge H), 7.0-7.7 (m, 6H, aromatic). Exact
mass: calcd. for $C_{14}H_{13}Br$ 260.0201; found,
260.0206.
Addition of Hydrogen Bromide to 1-Benzylidene-1H-
cyclobuta[de]naphthalene (25).

Hydrogen bromide was added to 1-benzylidene-1H-
cyclobuta[de]naphthalene (240 mg, 1 mmol) using the same
procedure and workup as that for 1-ethylidene-1H-
cyclobuta[de]naphthalene. The product was identified as
1-benzyl-1-bromo-1H-cyclobuta[de]naphthalene (66, 280 mg,
91%); ir(thin film, cm⁻¹) 3010, 2950, 1450, 1365, 1160,
1070, 775; nmr(CDCl₃, δ) 3.83(s, 2H, CH₂), 7.0-7.75(m,
11H, aromatic); exact mass: calcd. for C₁₈H₁₃Br 308.0201;
found, 308.0209.

1-(Diphenylmethylene)-1H-cyclobuta[de]naphthalene (67).

A suspension of 1-triphenylphosphonium-1H-cyclobuta-
[de]naphthalene bromide (1.44 g, 3 mmol) in anhydrous
tetrahydrofuran (30 ml) was cooled to -78° under nitrogen
and t-butyllithium (4 eq) was added via syringe. After
stirring 15 min, the red ylide was quenched by slow
addition of benzophenone (2 g) in tetrahydrofuran (10 ml),
The resulting solution was refluxed 30 hr, cooled, and
the solvent removed under reduced pressure. Passing the
residue through a short column of silica gel with hexane
gave 1-(diphenylmethylene)-1H-cyclobuta[de]naphthalene
(67, 640 mg, 70%) as white needles, mp 144-146; ir (KBr, cm\(^{-1}\)) 1560, 1460, 1370, 1140, 1060, 1010, 908, 736; 6.95 (d of d, 2H, J = 2 and 4 Hz, ortho on naphthalene ring), 7.15-7.8 (m, 14H, aromatic); exact mass: calcd. for C\(_{24}\)H\(_{16}\), 304.1252; found, 304.1260.

Anal. Calcd. for C\(_{24}\)H\(_{16}\): C, 94.70; H, 5.30.

Found: C, 94.78; H, 5.33.

Addition of Hydrogen Bromide to 1-(Diphenylmethylene)-1H-cyclobuta[de]naphthalene (67).

Hydrogen bromide gas was passed through a drying tube containing copper turnings and condensed in a trap (-78\(^\circ\)) containing 1-(diphenylmethylene)-1H-cyclobuta[de]-naphthalene (300 mg, 1 mmol) in methylene chloride (7 ml). Collection was continued until about 4 ml of hydrogen bromide had been condensed. The resulting blue solution was stirred at -78\(^\circ\) for 4 hr and warmed to room temperature in 8 hr as the excess hydrogen bromide evaporated. During this time the blue color disappeared and an orange color remained. Removal of the solvent under reduced pressure gave 1,2-diphenylacenaphthylene (68, 285 mg, 95%) as reddish orange needles, mp 161-163\(^\circ\) (from hexane), lit.\(^\text{16}\) 162-163\(^\circ\). The product exhibited a large molecular ion peak at 304 in the mass spectrum.
3'-Methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane]

Following the procedure of Card, 6 1-ethylidene-1H-cyclobuta[de]naphthalene (1.0 g, 6 mmol) dissolved in chloroform (15 ml) was added slowly to m-chloroperbenzoic acid (1.8 g, 9 mmol) in chloroform (25 ml) at 0°. The mixture was stored overnight in a refrigerator, then filtered, and washed with saturated sodium bicarbonate. The organic layer was dried with magnesium sulfate and the solvent removed to yield epoxide 70 (990 mg, 90%), identical to an authentic sample by nmr and tlc.

1-Acetyl-1H-cyclobuta[de]naphthalene (33).

Boron trifluoride-etherate (1 ml) in diethyl ether (20 ml) was added dropwise to epoxide 70 (550 mg, 3 mmol) in diethyl ether (100 ml) at -78°. The mixture was stirred vigorously while being kept at -30° for 2 hr at which time saturated aqueous sodium bicarbonate was added. The organic layer was dried and the solvent removed under reduced pressure to produce 1-acetyl-1H-cyclobuta[de]naphthalene (33, 510 mg, 93%), identical to an authentic sample by ir, nmr, and tlc.
Boron Trifluoride Catalyzed Rearrangement of 1-Acetyl-1H-cyclobuta[de]naphthalene (33).

Boron trifluoride-etherate (5 ml) was added to 1-acetyl-1H-cyclobuta[de]naphthalene (91 mg, 0.5 mmol) in diethyl ether (20 ml) and the mixture stirred for 3 hr at room temperature. After neutralizing the mixture with aqueous sodium bicarbonate, the ethereal layer was dried with magnesium sulfate and the solvent removed under reduced pressure. The product, 2-methylacenaphthenone (71, 85 mg, 93%), was identical to an authentic sample.

Reaction of 1H-Cyclobuta[de]naphthalene (1) with N-Bromosuccinimide.

Adapting the method of Card,6 1H-cyclobuta[de]-naphthalene (140 mg, 1 mmol) was dissolved in carbon tetrachloride (15 ml), azoisobutyronitrile (10 mg), and N-bromosuccinimide (270 mg, 1.5 mmol) were added and the mixture was refluxed for 24 hr. The solvent was removed under reduced pressure and the residue chromatographed on silica gel eluting with hexane to yield two fractions:

1) 1H-Cyclobuta[de]naphthalene (1, 73 mg, 52%), identical with an authentic sample.

2) 1-Bromo-1H-cyclobuta[de]naphthalene (4, 90 mg, 41%), identical with an authentic sample.
Reaction of 4-Nitro-1H-cyclobuta[de]naphthalene (42) with N-Bromosuccinimide.

Azoisobutyronitrile (10 mg) and N-bromosuccinimide (270 mg, 1.5 mmol) were added to 4-nitro-1H-cyclobuta[de]-naphthalene (185 mg, 1 mmol) in carbon tetrachloride (15 ml) and the mixture refluxed 12 hr. Thin-layer chromatography revealed only starting material, so more N-bromosuccinimide (300 mg) and azoisobutyronitrile (20 mg) were added and the mixture refluxed 36 hr. After cooling, the solution was filtered to remove the succinimide and the solvent removed under reduced pressure. 4-Nitro-1H-cyclobuta[de]naphthalene (42, 175 mg, 95%), identical with an authentic sample, was isolated.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (4) with N-Bromosuccinimide.

Using the same procedure and quantities as that for 4-nitro-1H-cyclobuta[de]naphthalene, 1-bromo-1H-cyclobuta-[de]-naphthalene (220 mg, 1 mmol) was reacted with N-bromosuccinimide with azoisobutyronitrile as initiator. The only significant product was 1-bromo-1H-cyclobuta[de]-naphthalene (4, 200 mg, 91%).
Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (4) with
N-Chlorosuccinimide.

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene
(220 mg, 1 mmol), N-chlorosuccinimide (265 mg, 2 mmol), and
azoisobutyronitrile (30 mg) in carbon tetrachloride (15 ml)
was refluxed 36 hr. Filtration and solvent removal left
1-bromo-1H-cyclobuta[de]naphthalene (4, 210 mg, 95%) as
the only product.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (4) with
t-Butyl Hypochlorite.

1-Bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol),
t-butyl hypochlorite (1 ml), and azoisobutyronitrile
(20 mg) in carbon tetrachloride (15 ml) were refluxed 16
hr. Volatiles were removed under reduced pressure and the
residue chromatographed on silica gel eluting with hexane
to give two fractions:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (4, 10 mg,
5%), identical with an authentic sample.

2) 1-Bromo-l-chloro-1H-cyclobuta[de]naphthalene (72,
225 mg, 89%), mp 104-106; ir(KBr, cm\(^{-1}\)) 1460, 1190,
1010, 990, 834, 782, 724; nmr(CDCl\(_3\), \(\delta\)) 7.20(d of
d, 2H, \(J = 5\text{Hz and 5Hz, ortho}\)), 7.54-7.62(m, 4H,
Free Radical Addition of Hydrogen Bromide to 1-Ethylidene-1H-cyclobuta[de]naphthalene (23).

Hydrogen bromide was passed through a drying tube containing copper turnings and bubbled into a carbon tetrachloride (50 ml) solution of 1-ethylidene-1H-cyclobuta[de]naphthalene (330 mg, 2 mmol) and azoisobutyronitrile (20 mg). The temperature of the solution rose from 24° to 29°. The addition of hydrogen bromide was continued for 20 min after the temperature had returned to 24°; then the solvent was removed under reduced pressure. The pale yellow oil that remained was identified as 1-(1-bromoethyl)-1H-cyclobuta[de]naphthalene (73, 450 mg, 91%), \( \text{ir(KBr, cm}^{-1}) 3010, 2950, 1600, 1460, 1440, 1370, 1175, 1050, 995, 805, 780; \) nmr(CDCl\(_3\), 6) 1.78(d, 3H, J = 6Hz, CH\(_3\)), 4.38 (d of q, 1H, J = 6Hz and 8.5Hz, -CHBr-), 5.40(d, 1H, J = 8.5Hz, bridge H), 7.09(d of d, 2H, J = 2Hz and 5Hz, ortho), 7.3-7.6(m, 4H, meta and para); exact mass: calcd. for C\(_{13}\)H\(_{11}\)Br, 246.0045; found 246.0051.
Photolytic Bromination of 1H-Cyclobuta[de]naphthalene (1H-CN).

1H-Cyclobuta[de]naphthalene (140 mg, 1 mmol) was dissolved in carbon tetrachloride (10 ml) and under the light of a 100 watt bulb bromine (180 mg, 1 mmol) in carbon tetrachloride (20 ml) was added slowly. After addition was complete, the solution was stirred 20 min under the light. Removal of the solvent under reduced pressure and chromatography on silica gel eluting with hexane gave two main fractions:

1) 1H-Cyclobuta[de]naphthalene (__, 50 mg, 36%), identical to an authentic sample.

2) 1α, 2α , 3α , 4α-Tetrabromo-1α,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (__, 180 mg, 39%), mp 119-121°C; ir(KBr, cm⁻¹) 1390, 1320, 1265, 1210, 1660, 1130, 1110, 952, 925, 895, 780, 732, 724, 700; nmr(CDCl₃, δ) 4.10 (broad s, 2H, CH₂), 4.76 (d, 1H, J = 2.5Hz, H on C₂), 5.03 (d, 1H, J = 9Hz, H on C₄), 5.42 (d of d, 1H, J = 2.5Hz and 9Hz, H on C₃), 6.9-7.6 (m, 3H, aromatic); exact mass: calcd. for C₁₁H₈Br₄, 455.7362; found, 455.7371.
Anal. Calcd. for C_{11}H_{8}Br_{4}: C, 28.73; H, 1.75.
   Found: C, 28.84; H, 1.88.

Reaction of Red-Al with 1α, 2β, 3β, 4α-Tetrabromo-1α, 2, 3, 4-tetrahydro-1H-cyclobuta[de]naphthalene (75).

1α, 2β, 3β, 4α-Tetrabromo-1α, 2, 3, 4-tetrahydro-1H-cyclobuta[de]naphthalene (360 mg, 0.8 mmol) was dissolved in dry ether (100 ml), Red-Al (10 ml, a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene) was added slowly, and the mixture was refluxed 16 hr. The excess hydride was decomposed with ethyl acetate and water. Then the organic layer was dried with magnesium sulfate and the solvent removed under reduced pressure to leave 1H-cyclobuta[de]naphthalene (1, 100 mg, 90%), identical with an authentic sample.

Elimination of 1α, 2β, 3β, 4α-Tetrabromo-1α, 2, 3, 4-tetrahydro-1H-cyclobuta[de]naphthalene (75).

A mixture of 1, 5-diazabicyclo[5.4.0]undec-5-ene (250 mg, 1.6 mmol) and 1α, 2β, 3β, 4α-tetrabromo-1α, 2, 3, 4-tetrahydro-1H-cyclobuta[de]naphthalene (230 mg, 0.5 mmol) in tetrahydrofuran (15 ml) was stirred at room temperature 1 hr, poured into pentane (200 ml), and passed through a
short column of silica gel. Removal of the solvent under reduced pressure left a white solid identified as 2,4-dibromo-1H-cyclobuta[de]naphthalene (79, 110 mg, 74%). An analytical sample was prepared by sublimation at 80° (0.1 mm) and recrystallization from hexane, mp 61-63°; ir (KBr, cm⁻¹) 1390, 1280, 1070, 1000, 855, 845, 770, 754; nmr(CDCl₃, δ) 4.63(s, 2H, CH₂), 7.02(d of d, 1H, J = 4Hz and 4Hz, ortho H), 7.20(s, 1H, H on C₃) 7.38-7.46(m, 2H, meta and para H); uv (λ, ε) 326 nm(350), 292(5245), 282 (5290), 235(31,000); exact mass: calcd. for C₁₁H₆Br₂, 295.8837; found, 295.8844.

Anal. Calcd. for C₁₁H₆Br₂: C, 44.34; H, 2.03.
Found: C, 44.25; H, 2.19.

Reduction of 2,4-Dibromo-1H-cyclobuta[de]naphthalene (79) with Red-Al.

2,4-Dibromo-1H-cyclobuta[de]naphthalene (150 mg, 0.5 mmol) was dissolved in dry diethyl ether (100 ml) and Red-Al (10 ml, a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene) was added dropwise. The solution was refluxed under nitrogen for 30 hr and the excess hydride decomposed with ethyl acetate and water. The organic layer was separated, dried with magnesium sulfate, and the solvent removed to yield 1H-cyclobuta[de]-naphthalene (1, 60 mg, 85%) as the only product, identical to an authentic sample.
Photolytic Bromination of 1-Bromo-1H-cyclobuta[de]-naphthalene (4).

Bromine (800 mg, 5 mmol) in carbon tetrachloride (20 ml) was added slowly under the light of a 100 watt bulb to 1-bromo-1H-cyclobuta[de]naphthalene (1.1 g, 5 mmol) in carbon tetrachloride (40 ml). After addition was complete, the mixture was stirred 30 min under the light, the solvent removed under reduced pressure, and the residue chromatographed on silica gel eluting with hexane. Two main fractions were separated:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (4, 510 mg, 46%), identical to an authentic sample.

2) 1,1a,2,3,4-Pentabromo-1a,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (81, 980 mg, 36%), two stereoisomers in the ratio of 4 to 1 partially separated by fractional recrystallization, mp (mixture) 144-146°; ir (mixture, KBr, cm⁻¹) 1460, 1390, 1160, 985, 890, 880, 850, 810, 785, 730; nmr (major isomer, CDCl₃, δ) 4.15(d, 1H, J = 11.5Hz, H on C₃), 5.49(d, 1H, J = 5Hz, H on C₄), 6.10(s, 1H, H on C₁), 7.05-7.7(m, 3H, aromatic); nmr (minor isomer, CDCl₃, δ) 4.82(d, 1H, J = 2.5Hz, H on C₂), 5.05(d, 1H, J = 8Hz, H on C₄), 5.59(d of
Base-Catalyzed Elimination of 1,1a,2,3,4-Pentabromo-1a,2,3,4-tetrahydro-1H-cyclobuta[de]naphthalene (81).

Pentabromides 81 (250 mg, 0.45 mmol) was dissolved in tetrahydrofuran (10 ml) and 1,5-diazobicyclo[5.4.0]-undec-5-ene (100 mg, 0.66 mmol) was added with stirring. The stirring was continued an additional hour, the solvent removed, and the residue chromatographed on silica gel eluting with hexane. The main fraction consisted of 2 inseparable compounds in the ratio of about 50/50. They are both of the general structure 84; the orientations of the bromines were undetermined. The total yield was (135 mg, 80%); mp(mixture) 104-108°C; ir(mixture, KBr, cm⁻¹) 1460, 1165, 1140, 1022, 1015, 780, 773, 695; nmr (CDCl₃, δ) 6.63(s, 1H, bridge H of one isomer), 6.70(s, 1H, bridge H of the other isomer), 7.17-7.69(m, 8H, aromatic); exact mass: calcd. for C_{11}H₇Br₅, 373.7943; found 373.7949.
Reaction of Pentabromide 81 with Zinc.

Zinc dust (65 mg, 1 mmol) was added to pentabromide 81 (300 mg, 0.56 mmol) in glacial acetic acid (2 ml) and diethyl ether (10 ml). The mixture was stirred 12 hr at room temperature, ether was added, and the solution filtered. After removal of the solvent under reduced pressure, the residue (105 mg) was analyzed by nmr. This revealed the products to be 1-bromo-1H-cyclobuta[de]-naphthalene (79%) and 1H-cyclobuta[de]naphthalene (12%).

Attempted Hydrolysis of 1-Bromo-1-chloro-1H-cyclobuta[de]-naphthalene (72).

A mixture of 1-bromo-1-chloro-1H-cyclobuta[de]-naphthalene (200 mg, 0.8 mmol), water (150 mg), potassium carbonate (200 mg) and tetrahydrofuran (10 ml) was stirred vigorously 12 hr at room temperature. Examination of the mixture by thin layer chromatography revealed no significant amount of reaction, so the mixture was refluxed for 36 hr. The solution was then dried with magnesium sulfate, filtered, and the solvent removed under reduced pressure. 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72, 192 mg, 96%) was obtained as the only product.
Hydrolysis of 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72).

A mixture of 1-bromo-1-chloro-1H-cyclobuta[de]-naphthalene (200 mg, 0.8 mmol), potassium hydroxide (50 mg), water (150 mg), and tetrahydrofuran (15 ml) was refluxed 48 hr and then poured into ether and acidified with hydrochloric acid. The ethereal layer was dried with magnesium sulfate and the solvent removed under reduced pressure. Chromatography of the residue on silica gel gave two main fractions:

1) 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72, 60 mg, 30%), identical with an authentic sample.
2) 1-Naphthoic acid (80 mg, 58%), identical with an authentic sample.

Reaction of p-Toluenesulfonyl Hydrazide with 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72).

1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (250 mg, 1 mmol) and p-toluenesulfonyl hydrazide (250 mg, 1.4 mmol) were dissolved in tetrahydrofuran (10 ml) and methanol (5 ml) and refluxed 24 hr. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel to give three main fractions:
1) 1H-Cyclobuta[de]naphthalene (1, 40 mg, 29%), identical to an authentic sample.

2) 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72, 85 mg, 34%), identical to an authentic sample.

3) Methyl 8-bromo-1-naphthoate (97, 17 mg, 10%), identical to an authentic sample by nmr, mass spectroscopy, and tlc.

Methanolysis of 1-Bromo-1-chloro-1H-cyclobuta[de]-naphthalene (72).

A mixture of 1-bromo-1-chloro-1H-cyclobuta[de]-naphthalene (125 mg, 0.5 mmol), methanol (10 ml), and sodium methoxide (100 mg) was refluxed 6 days. Vacuum removal of the solvent and chromatography on silica gel eluting with hexane and benzene gave:

1) 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72, 50 mg, 40%) identical to an authentic sample.

2) 1-Methylnaphthoate (99, 37 mg, 42%) identical to an authentic sample.
Reaction of Hydrazine with 1-Bromo-1-chloro-1H-cyclobuta-de]naphthalene (72).

1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (250 mg, 1 mmol) and hydrazine (300 mg) in tetrahydrofuran (15 ml) were refluxed 48 hr under nitrogen. Volatiles were removed under reduced pressure and finally by high vacuum at room temperature. Chromatography of the residue on silica gel gave:

1) 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72, 100 mg, 40%), identical with an authentic sample.

2) 1-Naphthaldehyde azine (91, 65 mg, 21%), identical with an authentic sample by mass spectroscopy, nmr, and tlc.

3) 9-Bromo-3H-benz[e]indazole (92, 30 mg, 12%), identical with an authentic sample (prepared by Bailey)\textsuperscript{8} by mass spectroscopy, nmr, and tlc.

The remainder of the material could not be identified.

Preparation of 1-Naphthaldehyde Azine.

1-Naphthaldehyde (310 mg, 2 mmol) in methanol (5 ml) was added to hydrazine (32 mg, 1 mmol), and stirred 1 hr. The yellow crystals (240 mg, 78%) of 1-naphthaldehyde azine (91) that formed were collected and washed with cold methanol, mp 154-156° (lit.\textsuperscript{46} 156-157°).
Reaction of 1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (72) with Silver Nitrate.

1-Bromo-1-chloro-1H-cyclobuta[de]naphthalene (130 mg, 0.5 mmol) was stirred vigorously in methanolic (150 ml) silver nitrate (300 mg). After 30 min, the solvent was removed under reduced pressure, the residue dissolved in ether, filtered, and the solvent removed to yield methyl-1-naphthoate (99, 80 mg, 86%), identical to an authentic sample.

Coupling of 1-Bromo-1H-cyclobuta[de]naphthalene (4) with Zinc/Silver.

Zinc activated with silver was prepared by refluxing powdered zinc (200 mg) with silver nitrate (30 mg) for 1 hr in distilled water (40 ml) in the dark. The metal was collected by filtration and washed with distilled water. The activated zinc, 1-bromo-1H-cyclobuta[de]-naphthalene (440 mg, 2 mmol), and distilled water (20 ml) were thus refluxed vigorously in the dark for 10 hr. After cooling, the mixture was extracted with ether, the ethereal layer dried with magnesium sulfate, and the solvent removed under reduced pressure. The residue was chromatographed on silica gel eluting with hexane to give two products:
1) 1H-Cyclobuta[de]naphthalene (1), 31 mg (11%), identical to an authentic sample.

2) 1,1′-Bi-1H-cyclobuta[de]naphthalene (101), 360 mg (65%), mp 135-137°; ir(KBr, cm⁻¹) 3050, 2940, 1605, 1475, 1215, 1010, 820, 785; nmr(CDC13, δ) 5.80 (s, 2H, bridge H), 6.90(d of d, J = 2Hz and 5.5Hz, 4H, ortho), 7.28-7.55(m, 8H, meta and para); C13 nmr (CDCl3, δ) 64.906(1C, C1), 116.378(2C, C2, γ), 121.692(2C, C4, 5), 125.712(1C, C9), 130.325(2C, C3, 6), 144.407(1C, C8), 145.486(2C, C1α, 7α); exact mass: calcd. for C22H14, 278.1095; found, 278.1104.


Found: C, 94.51; H, 5.47.

1-(1-Naphthylidene)-1H-cyclobuta[de]naphthalene (102).

A suspension of 1-triphenylphosphonium-1H-cyclobuta-[de]naphthalene bromide (1.44 g, 3 mmol) in anhydrous tetrahydrofuran (30 ml) was cooled to -78° under nitrogen treated with t-butyllithium (4.0 mmol). The resulting red solution was allowed to warm to room temperature and 1-naphthaldehyde (2 ml) was added via syringe. The solution was stirred 3 hr at room temperature, concentrated under vacuo to a light yellow oil, then passed through a short column of silica gel using hexane as
eluent. The yield of 1-(1-naphthylidene)-1H-cyclobuta-[de]naphthalene was 460 mg (83%). An analytical sample was prepared by recrystallization from hexane, mp 107-109°; ir(KBr, cm⁻¹) 3010, 1580, 1480, 1380, 1005, 808, 790, 770, 720(aromatic), 1690(C=C); nmr(CDCl₃, δ) 6.9-8.15(m, aromatic and olefinic H); exact mass: calcd. for C₂₂H₁₄', 278.1095; found, 278.1101.

Found: C, 94.62; H, 5.09.

Thermal Rearrangement of 1,1'-Bi-1H-cyclobuta[de]-naphthalene (101).

1,1'-Bi-1H-cyclobuta[de]naphthalene (140 mg, 0.5 mmol) was passed through a straight 30 cm pyrex tube heated to 430° at 0.1 mm of H₂. A yellow solid (90 mg, 64%) was collected in a trap cooled to -78°. Recrystallization from hexane gave a white solid identical to 1-(1-naphthylidene)-1H-cyclobuta[de]naphthalene (102) by nmr, mass spectroscopy, and melting point.

Bromination of 1-(1-Naphthylidene)-1H-cyclobuta[de]-naphthalene (102).

Bromine (340 mg, 2.1 mmol) in carbon tetrachloride (40 ml) was added dropwise to 1-(1-naphthylidene)-1H-cyclobuta[de]naphthalene (280 mg, 1.0 mmol) in carbon
tetrachloride (10 ml) at 0°. The solution was allowed to warm to room temperature and stirred an additional 1.5 hr. The solvent and excess bromine was removed under reduced pressure to yield 1-bromo-(bromomethyl-1-naphthyl)-1H-cyclobuta[de]naphthalene (103 410 mg, 94%). An analytical sample was prepared by recrystallization from hexane, mp 154-156°; ir(KBr, cm⁻¹) 1600, 1505, 1450, 1190, 1155, 1120, 1040, 995, 910, 775, 720; nmr(CDCl₃, δ) 6.69 (s, 1H, benzylic H), 6.85-8.2 (m, 13H, aromatic H); exact mass: calcd. for C₂₂H₁₄Br₂, 435.9463; found, 435.9472.


Found: C, 60.10; H, 3.29.
Δ1,1'-Bi-1H-cyclobuta[de]naphthalene (104). 48

Zinc activated with silver was prepared as previously described. The zinc (50 mg) was suspended in a solution of 1-bromo-1-chloro-1H-cyclobuta[de]naphthalene (256 mg, 1 mmol) in tetrahydrofuran (15 ml). This mixture was refluxed 10 hr, cooled, filtered, and the solvent removed under reduced pressure. Examination of the residue by tlc revealed a complex mixture (6-8 components). The two major fractions were isolated by chromatography on silica gel eluting with hexane:

1) 1H-Cyclobuta[de]naphthalene (1), 20 mg (14%), identical to an authentic sample.

2) Δ1,1'-Bi-1H-cyclobuta[de]naphthalene (104), 40 mg (29%), ir (KBr, cm⁻¹) 1560, 1460, 1380, 1140, 1060, 1005, 910, 740; nmr (CDCl₃, δ) 7.31 (d of d, H, J = 2 Hz and 4 Hz, ortho), 7.55–7.7 (m, H, meta, and para); C¹³ nmr (CDCl₃, δ) 114.6 (2C, C₂, 7), 122.3 (2C, C₄, 5), 125.7 (1C, C₉) 131.15 (2C, C₃, 6), 143.7 (1C, C₈), 144.2 (2C, C₁a, 7a), 149.7 (1C, C₁); exact mass: calcd. for C₂₂H₁₂ 276.0939, found 276.0943. An analytical sample was prepared by preparative tlc, mp 191–195°.


Found: C, 95.07; H, 4.37.
Alternate Synthesis of $\Delta^1,1'$-Bi-$1H$-cyclobuta[de]naphthalene (104).

$1,1'$-Bi-$1H$-cyclobuta[de]naphthalene (278 mg, 1 mmol), t-butylhypochlorite (110 mg, 1 mmol), and azoisobutyronitrile (10 mg) in carbon tetrachloride (15 ml) was refluxed vigorously 6 hr. Removal of the volatiles left 1-chloro-$1,1'$-bi-$1H$-cyclobuta[de]naphthalene as the major product. The naphthalene was identified by nmr (CDCl$_3$, δ) 5.80(s, 1H, bridge H), 6.8-7.6(m, 12H, aromatic) and mass spectroscopy (peaks at 312, 314) and then was used for the next step.

Lithium diisopropylamide (1 mmol, prepared from 1.1 eq n-butyllithium and 100 mg diisopropyl amine at -78°) was added to 1-chloro-$1,1'$-bi-$1H$-cyclobuta[de]naphthalene (~ 310 mg, 1 mmol) in tetrahydrofuran (15 ml) at 0°. This solution was stirred 3 hr at room temperature, then the solvent and amine were removed under reduced pressure. Chromatography of the residue on silica gel with hexane gave $\Delta^1,1'$-bi-$1H$-cyclobuta[de]naphthalene (104, 65 mg, 24%), identical with an authentic sample.

The elimination was also effected with $1,5$-diazabicyclo-[5.4.0]undec-5-ene (150 mg, 1 mmol) in refluxing tetrahydrofuran (10 ml). After purification of the product the
yield of $\Delta^1,1'-\text{bi-1H-cyclobuta}[de]\text{naphthalene}$ was 57 mg (21%).

1-Methylene-1H-cyclobuta[de]naphthalene (22), 1-Ethylene-1H-cyclobuta[de]naphthalene (23), 1-Benzilidene-1H-cyclobuta[de]naphthalene (25), and 1-Isopropylidene-1H-cyclobuta[de]naphthalene (24).

Olefins 22, 23, and 25 were prepared in yields of 80-85% by the method of Card from 1-triphenylphosphonium-1H-cyclobuta[de]naphthalene bromide, t-butyllithium, and the respective aldehydes (paraformaldehyde, acetaldehyde, and benzaldehyde) in tetrahydrofuran.

The 1-isopropylidene-1H-cyclobuta[de]naphthalene used in subsequent reactions was prepared by Card.6

Diels-Alder Reaction of 1-Methylene-1H-cyclobuta[de]-naphthalene (22) with Tetraphenylcyclopentadienone.

A solution of 1-methylene-1H-cyclobuta[de]naphthalene (152 mg, 1 mmol) and tetraphenylcyclopentadienone (385 mg, 1 mmol) in xylene (15 ml) was refluxed 16 hr. After removal of the solvent, the residue was chromatographed on silica gel eluting with hexane-benzene to give three fractions:
1) 1-Methylene-1H-cyclobuta[de]naphthalene (22; 30 mg, 20%), identical to an authentic sample.

2) 1',4',5',6'-Tetraphenylspiro[1H-cyclobuta[de]-naphthalene-1,2'-[5]norbornen]-7'-one, (106, 370 mg, 69%), mp 122-126; ir(KBr, cm⁻¹) 1760 (C=O), 3010, 2970, 1590, 1470, 1410, 1360, 1245, 1050, 890, 760; nmr(CDCl₃, δ) 6.65-8.0(m, 28H, aromatic and methylene H); exact mass (on minus C=O peak): calcd for C₄₀H₂₈, 508.2191; found, 508.2201.

   Found: C, 92.06; H, 5.62.

3) Tetraphenylcyclopentadienone (90 mg, 23%), identical to an authentic sample.

Attempted Diels-Alder Reactions of 1-Ethylidene-1H-cyclobuta[de]naphthalene (23), and 1-Isopropylidene-1H-cyclobuta[de]naphthalene (24).

1-Ethylidene-1H-cyclobuta[de]naphthalene (166 mg, 1 mmol) and 1-isopropylidene-1H-cyclobuta[de]naphthalene (180 mg, 1 mmol) were each dissolved in solutions of tetraphenylcyclopentadienone (385 mg, 1 mmol) in xylene (15 ml) and refluxed 24 hr. In each case after solvent removal only the starting olefin (> 90%) and tetraphenylcyclopentadieneone were isolated.
Spiro[1H-cyclobuta[de]naphthalene-1,1'-cyclopropane] (107).

Powdered zinc (200 mg) was heated in a solution of cupric acetate (50 mg) in acetic acid (15 ml) until the blue color disappeared (~1 hr). The activated zinc was filtered, washed with acetic acid then ether (250 ml), and quickly suspended in dry diethyl ether (50 ml). Diiodomethane (540 mg, 2 mmol) was added and the mixture was refluxed 2 hr under nitrogen, at which time 1-methylene-1H-cyclobuta[de]naphthalene (200 mg, 1.3 mmol) was added and the suspension refluxed 12 hr. Filtration and removal of volatiles under vacuum left spiro[1H-cyclobuta[de]-naphthalene-1,1'-cyclopropane] (107, 180 mg, 82%) as a clear oil. Vacuum distillation gave an analytical sample bp 135-140°C/0.1 mm, ir(film, cm⁻¹) 3010, 1470, 1200, 1050, 795, nmr(CDCl₃, δ) 1.53(s, 4H, CH₂), 6.88 (d of d, 2H, J = 2Hz and 4Hz, ortho), 7.4-7.65(m, 4H, meta and para); exact mass: calcd. for C₁₃H₁₀, 166.0782; found, 166.0786.

Anal. Calcd. for C₁₃H₁₀: C, 93.94; H, 6.06.
Found: C, 93.58; H, 6.22.

1-Cyano-1H-cyclobuta[de]naphthalene (108).

Dry potassium cyanide (500 mg) was added to 1-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) and 18-crown-6
ether (300 mg) in acetonitrile (15 ml) and the mixture stirred vigorously at room temperature for 12 days. The dark solution was worked up by pouring into water, extracting with ether, drying the ethereal layer with magnesium sulfate, and removing the solvent under reduced pressure. The residue was passed through a short column of silica gel eluting with benzene to give 1-cyano-1H-cyclobuta[de]-naphthalene (108) 140 mg, 85%), mp 127.5-129.5°; ir(KBr, cm⁻¹) 2250(C≡N), 1490, 1280, 1115, 1050, 825, 795 (aromatic); nmr 5.81(s, 1H, bridge), 7.25(d of d, 2H, J = 2 and 5 Hz, ortho), 7.5-7.7(m, 4H, meta and para); C¹³ nmr (CDCl₃, δ) 45.684(1C, C₁), 117.342(2C, C₂, 7), 123.314 (2C, C₄, 5), 126.130(1C, C₉), 131.130(2C, C₃, 6), 137.005 (1C,C₈), 146.423(2C, C₁₈, 7a); exact mass: calcd. for C₁₂H₇N, 165.0578; found, 165.0582.


Basic Hydrolysis of 1-Cyano-1H-cyclobuta[de]naphthalene (108).

1-Cyano-1H-cyclobuta[de]naphthalene (55 mg, 0.33 mmol), sodium hydroxide (0.1 g), water (20 ml), and ethanol
(20 ml) were refluxed 2.5 hr. The mixture was then acidified, extracted with ether, the ethereal layer dried with magnesium sulfate, and the solvent removed under reduced pressure. The residue was passed through a short column of silica gel eluting with benzene to yield after solvent removal 1H-cyclobuta[de]naphthalene-1-carboxylic acid (20 mg, 32%), identical to an authentic sample.

Reaction of Methyl Magnesium Bromide with 1-Cyano-1H-cyclobuta[de]naphthalene (108).

Methyl magnesium bromide (2 ml of a 1.3M solution in diethyl ether) was added via syringe to 1-cyano-1H-cyclobuta[de]naphthalene (250 mg, 1.5 mmol) in dry tetrahydrofuran (25 ml). After refluxing this solution 12 hr under nitrogen, the excess Grignard reagent was quenched by slow addition of 10% hydrochloric acid. After additional 10% hydrochloric acid (50 ml) had been added, the mixture was refluxed 3 hr, neutralized with sodium bicarbonate, extracted with ether, and the ethereal layer dried with magnesium sulfate. After removal of the solvent, chromatography on silica gel eluting with benzene gave 1H-cyclobuta[de]naphthalen-1-yl methyl ketone (33), 50 mg (18%), as the only identifiable product. The ketone 33 was identical to an authentic sample by nmr and ir.
9-Bromofluorene

N-Bromosuccinimide (2.0 g, 11 mmol) and azoisobutyronitrile (50 mg) were added to fluorene (1.7 g, 10 mmol) in carbon tetrachloride (100 ml) and the mixture was refluxed for 12 hr. After cooling, the solution was filtered and the solvent removed under reduced pressure to yield 9-bromofluorene (2.2 g, 86%), mp 101-104 (lit. 104-105). The nmr absorption at δ 5.96 (s, 1H, H on C9) matched the literature.

9-Cyanofluorene (110).

Refluxing a mixture of 9-bromofluorene (2.2 g, 8.6 mmol), potassium cyanide (5 g), and 18-crown-6 ether (50 mg) in acetonitrile (100 ml) for 12 hr, addition of water and extraction with ether produced, after drying and removal of the solvent, 9-cyanofluorene (110, 140 mg, 85%), mp 149-151 (lit. 151-152). The nmr absorption at δ 4.92 (s, 1H, H on C9) corresponded to the literature.

Relative Rates of Deuterium Exchange of 1-Cyano-1H-cyclobuta[d,e]naphthalene (108), 9-Cyanofluorene (110), and Diphenylacetonitrile (111).

Each nitrile (0.10 mmol) was dissolved in t-butanol-0-d (0.50 ml), placed in an nmr tube, and a reference
spectrum was taken immediately. A standard base solution (0.50 ml of a solution of 200 μl triethylamine in 2.0 ml t-butanol-0-d) was then added to each of the three sample tubes. The progress of the reaction at 20° was monitored by nmr at selected time intervals (see Table 4).

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene with Potassium Nitrite.

1-Bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) was dissolved in acetonitrile (25 ml) containing 18-crown-6 (500 mg) and reacted with potassium nitrite (1 g) using two different procedures. The first was stirring at room temperature for 14 days and the second involved refluxing for 2 hr. Both reaction mixtures were worked up by filtering the potassium salts and removing the solvent under reduced pressure. The residue was passed through a short column of silica gel eluting with benzene to remove the crown ether. For both procedures the only identifiable product was 1-naphthaldehyde (~110 mg, 72%), identical to an authentic sample by nmr, ir, and mass spectrum.
l-Chloro-lH-cyclobuta[de]naphthalene (II2).

l-Bromo-lH-cyclobuta[de]naphthalene (220 mg, 1.0 mmol), acetonitrile (50 ml), potassium chloride (1 g), and 18-crown-6 ether (20 mg) were refluxed for 10 days, then poured into water and extracted with ether. The ethereal layer was dried with magnesium sulfate, and the solvent removed under reduced pressure to yield l-chloro-lH-cyclobuta[de]naphthalene (II2, 155 mg, 89%). An analytical sample was prepared by sublimation at 50° (0.3 mm), mp 65-67°; ir(KBr, cm⁻¹) 1270, 1210, 1030, 990, 795, 782, 745, 718; nmr(CDCl₃, δ) 6.77(s, 1H, bridge), 7.18(d of d, 2H, J = 5 and 2Hz, ortho), 7.3-7.7(m, 4H, meta and para); C¹³ nmr (CDCl₃, δ) 66.050(1C, C₁), 115.934 (2C, C₂,γ), 123.023(2C, C₄,₅), 126.251(1C, C₉), 131.276 (2C, C₃,δ), 143.729(2C, C₁₈,₇a), 145.282(1C, C₈); exact mass: calcd. for C₁₁H₇Cl, 174.0236; found, 174.0240.


Found: C, 75.57; H, 4.02.

Reaction of l-Bromo-lH-cyclobuta[de]naphthalene (2) with Benzyltriethylammonium Chloride.

A solution of l-bromo-lH-cyclobuta[de]naphthalene (220 mg, 1 mmol) and benzyltriethylammonium chloride (2 g)
in chloroform (50 ml) were refluxed 9 days. The mixture was then poured into water, the organic layer dried with magnesium sulfate, and the solvent removed under reduced pressure. The residue was dissolved in hexane, filtered to remove insoluble material, and the solvent removed to leave 1-chloro-1H-cyclobuta[de]naphthalene (112, 160 mg, 92%) identical with an authentic sample.

1H-Cyclobuta[de]naphthalen-1-yl p-Toluenesulfonate (19). Tosylate 19 was prepared similar to the method of Card6 by heating 1-bromo-1H-cyclobuta[de]naphthalene (1.0 g, 4.5 mmol) and silver tosylate (1.7 g, 6 mmol) in hexamethylphosphoramide (20 ml) at 90° for 24 hr. The yield was 0.95 g (67%) and 19 was identical to an authentic sample.

1-Iodo-1H-cyclobuta[de]naphthalene (16). Card's procedure6 of refluxing a mixture of 1-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol), potassium iodide (1 g), and 18-crown-6 ether (20 mg) in acetonitrile (30 ml) for 24 hr produced 1-iodo-1H-cyclobuta[de]-naphthalene (16, 250 mg, 94%), identical to an authentic sample.
Lithium dimethyl cuprate was generated by adding methyl lithium (20 mmol) to a suspension of cuprous iodide (2 g, 10 mmol) in dry diethyl ether at 0°C. After stirring the cuprate solution 15 min at 0°C, tosylate (~310 mg, 1 mmol) dissolved in ether was added slowly and the resulting mixture stirred 30 hr at room temperature. The excess cuprate was decomposed by slowly adding water. Then the mixture was extracted with ether, the ethereal layer was dried with magnesium sulfate, and the solvent removed under reduced pressure to leave 1-methyl-1H-cyclobuta[de]naphthalene (32, 110 mg, 71%), identical to an authentic sample by mass spectroscopy and nmr.

Lithium dimethyl cuprate was generated as previously described and reacted with 1-chloro, 1-bromo, and 1-iodo-1H-cyclobuta[de]naphthalene, respectively. The same scale, procedure, and workup were used as for tosylate 19. In all 3 cases 1-methyl-1H-cyclobuta[de]naphthalene was
formed. The respective yields were 13%, 10%, and 6%. The remainder of the products remained unidentified.

Reaction of Lithium Divinyl Cuprate with 1H-Cyclobuta[de]-naphthalen-1-yl p-Toluensulfonate (19).

Magnesium (1.5 g, 60 mmol) was placed in a flask fitted with a dry ice condenser and containing dry ether (150 ml). Vinyl bromide (11 g, 100 mmol) was added slowly under nitrogen and the solution stirred vigorously until all the magnesium disappeared; then diphenyldichlorotin (7 g, 20 mmol) was added and the solution heated 18 hr at 40°. Excess Grignard was quenched with aqueous ammonium chloride, the ethereal layer was dried with magnesium sulfate, and the solvent removed under reduced pressure.

The product, diphenyldivinyltin, was treated with phenyllithium (35 mmol) in dry ether (150 ml) at room temperature under nitrogen according to known procedure. The expected precipitate of tetraphenyltin formed immediately, indicating the production of vinylvllithium.

Lithium divinyl cuprate \(^{28}\) was prepared by adding cuprous bromide (2.42 g, 17 mmol) to the vinylvllithium solution at \(-10^\circ\) and stirring the mixture 30 min. 1H-Cyclobuta[de]naphthalen-1-yl p-toluensulfonate (610 mg, 2 mmol) in diethyl ether (30 ml) was added to the cuprate
solution and the mixture stirred 24 hr at room temperature. The excess cuprate was quenched with water, the ethereal layer was dried, and the solvent removed to leave an oily brown residue. Tlc and nmr revealed a large number of products, none of which could be identified as the desired hydrocarbon, 1-vinyl-1H-cyclobuta[de]naphthalene (113).

**Attempted Isomerization of 1-Ethylidene-1H-cyclobuta[de]naphthalene (23).**

1-Ethylidene-1H-cyclobuta[de]naphthalene (83 mg, 0.5 mmol) dissolved in dry tetrahydrofuran (15 ml) was cooled to -78° and under nitrogen treated with t-butyllithium (0.55 mmol). After stirring 20 min at -78°, deuterium oxide (2 ml) was added via syringe and the solution allowed to warm to room temperature. Ether was added, the ethereal layer dried with magnesium sulfate, and the solvent removed to leave a pale yellow oil (75 mg, 90%). The product was identified as 1-(ethylidene-2-d)—1H-cyclobuta[de]naphthalene by nmr (CDCl₃, 6) 2.0(d, 2H, J = 6.5Hz, -CH₂D), 5.8(t, 1H, J = 6.5Hz, olefinic), 6.9-7.6(m, 6H, aromatic); and by a large mass spectrum peak at 167.

Using the same procedure except quenching with water instead of deuterium oxide gave 1-ethylidene-1H-cyclobuta-[de]naphthalene (~90%, identical to an authentic sample.
Elimination Reactions of 1-(1-Bromoethyl)-1H-cyclobuta[de]naphthalene (74).

1-(1-Bromoethyl)-1H-cyclobuta[de]naphthalene (125 mg, 0.5 mmol) dissolved in tetrahydrofuran (10 ml) at -78° was treated with a solution of 1,5-diazobicyclo[5.4.0]undec-5-ene (90 mg, 0.6 mmol) in tetrahydrofuran (10 ml). The mixture was warmed to room temperature and stirred an additional 6 hr. Then the solvent was removed under reduced pressure, the residue taken up in pentane, this solution filtered, and the solvent removed to yield 1-ethylidene-1H-cyclobuta[de]naphthalene (23, 75 mg, 90%); identical to an authentic sample.

1-(1-Bromoethyl)-1H-cyclobuta[de]naphthalene was also reacted with potassium triethyl carbinoxide (0.5 mmol made from 20 mg potassium and 58 mg triethyl carbinol in 10 ml dry tetrahydrofuran) and with lithium 2,2,6,6-tetramethylpiperidide (0.5 mmol made from 0.5 eq t-butylithium and 70 mg of the piperidine at 0° in 10 ml dry tetrahydrofuran) using the same procedure and workup as in the first case. With the last two bases only one product was isolated, 1-ethylidene-1H-cyclobuta[de]naphthalene (23, ~90%); identical to an authentic sample.

Solutions of p-toluenesulfonylhydrazide (550 mg, 3 mmol) in ethanol (3 ml) and 1-acetyl-lH-cyclobuta[de]-naphthalene (560 mg, 3 mmol) in ethanol (3 ml) were mixed and refluxed 2 hr. Cooling caused a white solid to precipitate which was collected by filtration. The yield of 1-acetyl-lH-cyclobuta[de]naphthalene p-toluenesulfonyl-hydrazone was 760 mg (69%). Recrystallization from ethanol gave an analytical sample, mp 172-174°; nmr (δ, CDCl₃) 1.76(s, 3H, -C-CH₃), 2.45(s, 3H, tosyl CH₃), 5.93 (s, H, bridge H), 7.0-7.95(m, 10H, aromatic); exact mass: calcd. for C₂₀H₁₈N₂S₀₂, 350.1089; found, 350.1094.

Found: C, 68.31; H, 5.26.

Reaction of 1-Acetyl-lH-Cyclobuta[de]naphthalene p-Toluenesulfonylhydrazone (118) with Two Equivalents of Alkylithium.

A solution of 1-acetyl-lH-cyclobuta[de]naphthalene p-toluenesulfonylhydrazone (350 mg, 1 mmol) in dry tetrahydrofuran (25 ml) was treated with t-butylolithium (2.1 eq) at -78° under nitrogen and the mixture was stirred
24 hr at room temperature. After quenching of the reaction with water the organic layer was dried and the solvent removed under reduced pressure. Passing the residue through a short column of silica gel with hexane produced 1-ethylidene-1H-cyclobuta[de]naphthalene (23, 35 mg, 21%), identical to an authentic sample by ir and nmr. The remainder of the material could not be identified.

1-(2-Hydroxyethyl)-1H-cyclobuta[de]naphthalene (119).

t-Butyllithium (1.1 eq) was added via syringe to a cold (-78°) solution of 1-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) in dry tetrahydrofuran (50 ml). After stirring 10 min under nitrogen, ethylene oxide (5 ml, bp 10-11°) was added dropwise and the solution brought to room temperature over several hours. Removal of the volatiles under reduced pressure left a light brown oil whose chromatography on silica gel with hexane-benzene gave two major components:

1) 1H-Cyclobuta[de]naphthalene (1, 25 mg, 18%), identical to an authentic sample.

2) 1-(2-Hydroxymethyl)-1H-cyclobuta[de]naphthalene (119, 95 mg, 51%); ir(film, cm⁻¹) 3400(OH), 3100, 2960, 1470, 1200, 1040, 780, 672; nmr(CDCl₃, δ) 1.96(broad s, 1H, OH), 2.30(q, 2H, J = 6Hz, CH₂
attached to bridge), 3.85 (t, 2H, J = 6Hz, CH₂ near hydroxyl), 5.32 (t, 1H, J = 6Hz, bridge), 7.07 (d of d, 2H, J = 2Hz and 4Hz, ortho), 7.2–7.7 (m, 4H, meta and para), exact mass: calcd. for C₁₃H₁₂O, 183.0810; found, 183.0815.

Anal. Calcd. for C₁₃H₁₂O: C, 84.75; H, 6.57.

Found: C, 84.38; H, 6.51.
REFERENCES


33. Values obtained from authentic samples.


43. The basic procedure was obtained as a private communication from Dr. B. Snow.


46. *Beil.*, 7, 400.


49. The nitrile carbon is apparently buried under the 117 peak.


PART II: SYNTHESIS OF CYCLOPROPENES

INTRODUCTION

The purpose of this study was to develop a mild general method for synthesis of cyclopropenes.

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

The development of the synthesis was very successful, but the study was terminated due to the publication of closely parallel work.\footnote{1}
HISTORICAL

Efficient methods for preparing cyclopropenes are limited at present. The various methods that have been described are in general terms: 1) cyclization of an acyclic molecule, 2) addition to an acetylene, and 3) introduction of unsaturation into a cyclopropane. An example of the first method is the decomposition of the diazo compound (1) derived from mesityl oxide to give 1,3,3-trimethylcyclopropene (2) either directly or via intermediate pyrazoline 3 (Equation 1).\(^2,3\) Addition of diphenyl diazo methane to acetylene forms 5,5-diphenyl pyrazoline (4) whose photolysis gives 3,3-diphenylcyclopropene (5, Equation 2).\(^4\)
Thermal or photolytic generation of cycloheptatrienyldiene (6) and its addition to phenylacetylene illustrates another cyclopropene synthesis (Equation 3).

Reaction of excess 2-lithio-3-methyl-2-butene (7) with dichloromethane yields 1,3,3-trimethylcyclopropene (2) via capture of monochlorocarbene and subsequent rearrangement (Equation 4).

Dehydrohalogenation can be accomplished on a halocyclopropane if the cyclopropene generated is exceptionally stable such as tetrachlorocyclopropene (8, Equation 5).
A mild method for introducing unsaturation in a carbon skeleton involves β elimination of β-haloalkylsilanes (9) with potassium fluoride in dimethylsulfoxide (Equation 6). 8

\[
\text{SiMe}_3 \quad \text{F}^{-} \quad \text{R}_2\text{C} - \text{CR}_2 \quad \rightarrow \quad \text{R}_2\text{C} = \text{CR}_2
\]

The elimination also works well for preparing alkynes from β-haloalkenylsilanes (10, Equation 7). 9

\[
\text{Me}_3\text{Si} = \text{C} = \text{C} - \text{H} \quad \text{F}^{-} \quad \text{H} - \text{C} = \text{C} - \text{H} + \text{FSiMe}_3
\]

Trans and cis-β-haloalkenylsilanes each react to give acetylenes, but the trans olefin eliminates significantly faster. A major driving force for these reactions is the strength of the fluorine-silicon bond formed. Other highly strained species then can be produced by this
elimination method include allenes (11, Equation 8)¹⁰ and allene oxides (12, Equation 9).¹¹

\[ \text{SiR}_3 \xrightarrow{F^-} \text{C} = \text{C} \]

\[ \text{SiR}_3 \xrightarrow{F^-} \text{O} \]

¹⁰

¹¹
RESULTS AND DISCUSSION

Knowing that various highly strained molecules are produced by the fluoride ion elimination of appropriate β-halosilanes, it seemed possible that cyclopropenes could be synthesized by a similar elimination of 1-halo-2-trimethylsilylcyclopropenes.

A study was undertaken to prepare 1,1-dihalo-2,2,3-trimethyl-3-trimethylsilylcyclopropanes (13 and 14). These cyclopropanes were chosen since 13 and 14 have halogens both cis and trans to the trimethylsilyl group. In this way either syn and anti elimination can be accommodated. Also the cyclopropanes that would result by reaction with fluoride ion are tetrasubstituted and should be reasonably stable.
Bromination of 2-methyl-2-butene (15) and treatment of the resulting dibromide with alkali yields 2-bromo-3-methyl-2-butene (16) as the major product (Equation 10).

\[ \text{H}_3\text{C} = \text{CH}_3 \xrightarrow{1) \text{Br}_2} \text{H}_3\text{C} - \text{Br} \xrightarrow{2) \text{KOH}} \text{H}_3\text{C} - \text{CH}_3 \]

The isolated yield (38%) was low due to the presence of minor products and the lengthy distillations required to obtain a pure sample. Formation of the Grignard reagent from 16 and reaction with chlorotrimethylsilane affords 2-methyl-3-trimethylsilyl-2-butene (17, 37%, Equation 11).

\[ \text{Mg} \xrightarrow{1) \text{Mg}} \text{H}_3\text{C} = \text{CH}_3 \xrightarrow{2) \text{Cl-SiMe}_3} \text{H}_3\text{C} - \text{Si(CH}_3\text{)}_3 \]

The identity of 17 is confirmed by spectral properties (notably a pmr singlet at $\delta$ 0.05 for the trimethylsilyl protons and a multiplet at $\delta$ 1.50-1.65 for the olefinic methyl groups) and combustion analysis. The electron
density in the carbon-carbon double bond of 17 is fairly high since long range nmr coupling occurs between the methyl groups on the double bond, while all the methyl groups of bromide 16 are singlets.

Dichlorocarbene, from chloroform and aqueous hydroxide using a phase transfer catalyst, adds readily to vinylsilane 17 (76%, Equation 12).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Si}(\text{CH}_3)_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
x & \quad x \\
x & \quad \text{X} = \text{Cl, 13} \\
& \quad \text{Br, 14}
\end{align*}
\]

Potassium t-butoxide and bromoform produce dibromocarbene which also adds to vinylsilane 17 (42%, Equation 12).

The structures of 1,1-dichloro-2,2,3-trimethyl-3-trimethylsilylcyclopropane (13) and 1,1-dibromo-2,2,3-trimethyl-3-trimethylsilylcyclopropane (14) are assigned from their spectra and their satisfactory elemental analyses. The nmr absorptions for 13 are singlets at \( \delta 1.10, 1.15, \) and 1.33 for the three methyl groups and a
singlet at $\delta$ 0.20 for the trimethylsilyl group. The similar absorptions for 14 are $\delta$ 1.08, 1.14, 1.31 and 0.22.

Reactions of 13 and 14 with potassium fluoride in dimethylsulfoxide for 24 hr at room temperature give 1-chloro-2,3,3-trimethylcyclopropene (18, 61%) and 1-bromo-2,3,3-trimethylcyclopropene (19, 59%, Equation 13), respectively.

\[
\text{Si}(\text{CH}_3)_3 \xrightarrow{\text{F}^-} \begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\]

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

$X = \text{Cl, } 13$

$X = \text{Br, } 14$

Use of 18-crown-6 ether greatly improves the elimination reaction giving yields of 84% and 81% for 18 and 19 in 12 hr at room temperature.

The structures of 18 and 19 were assigned by their spectral properties, exact mass, and combustion analyses. The nmr signals of 18 are $\delta$ 1.70 (s, 6H, gem CH$_3$) and 1.77
(s, 3H, vinyl CH$_3$); the signals for 19 are $\delta$ 1.69 and 1.75.

This new synthesis of cyclopropanes gives excellent yields under mild conditions.
EXPERIMENTAL

2-Bromo-3-methyl-2-butene (16).

Following a known procedure,\textsuperscript{12} 2-methyl-2-butene (70 g, 1.0 mol) in anhydrous diethyl ether (500 ml) was cooled to 0\textdegree and bromine (160 g, 1.0 mol) was added slowly in the dark. Removal of the solvent under reduced pressure left 2',3-dibromo-2-methylbutane (~ 230 g, 100%).

A solution of potassium hydroxide (70 g, 1.25 mol) in ethanol (350 ml) and water (40 ml) was heated to reflux. The crude 2,3-dibromo-2-methylbutane (230 g) was added at such a rate that reflux was maintained without external heat. The mixture was then heated for 6 hr, cooled, and vacuum filtered to remove the potassium bromide. This solution was poured into water (1500 ml) and the bottom layer removed and dried with magnesium sulfate. Two fractional distillations through a 30 cm glass helix column gave 2-bromo-3-methyl-2-butene (16, 54 g, 38%), bp 116-122\textdegree (lit.\textsuperscript{12} 116-122\textdegree). The nmr (CCl\textsubscript{4}, \delta) of 16 matched the literature\textsuperscript{12} 1.72(s, 3H, CH\textsubscript{3}), 1.80(s, 3H, CH\textsubscript{3}), 2.21(s, 3H, CCH\textsubscript{3}Br).
2-Methyl-3-trimethylsilyl-2-butene (17).

Magnesium turnings (10 g, 0.41 mol), 1,2-dibromo-ethane (1 ml), and dry tetrahydrofuran (15 ml) were mixed and, when the reaction commenced, 2-bromo-2-butene (54 g, 0.38 mol) in tetrahydrofuran (160 ml) was added at a rate that maintained reflux. After refluxing an additional 1 hr, the solution was cooled to 0° and chlorotrimethylsilane (90.0 g, 0.83 mol) was added and the solution stirred overnite at room temperature. The mixture was filtered, the liquid concentrated (70 ml) under reduced pressure, and the residue fractionally distilled to yield 2-methyl-3-trimethylsilyl-2-butene (17, 20 g, 37%), bp 135-140° or 30-40°/10 mm; ir(film, cm^{-1}) 2950, 1610, 1430, 1230, 840, and 755; nmr (CCl_{4}, 6) 0.05(s, 9H, Si(CH_{3}) and 1.50-1.65(m, 9H, methyls); m/e 142, 127, 73; an analytical sample was prepared by preparative gc at 125°.

Anal. Calcd. for C_{8}H_{18}Si: C, 67.55; H, 12.67.

Found: C, 67.32; H, 12.52.

1,1-Dichloro-2,2,3-trimethyl-3-trimethylsilylcyclopropane (13).

Benzyltriethyl ammonium chloride (500 mg) was added to a mixture of sodium hydroxide (12 g, 0.3 mol) in water
(50 ml) and 2-methyl-3-trimethylsilyl-2-butene (10 g, 0.07 mol) in chloroform (50 ml). The two phase system was then stirred vigorously for 36 hr. The organic layer was washed with water (1000 ml) and then dried with magnesium sulfate. Removal of the solvent and vacuum distillation gave 1,1-dichloro-2,2,3-trimethyl-3-trimethylsilylcyclopropane (13, 12 g, 76%), bp 75-80°/2 mm; ir(film, cm⁻¹) 2920, 1460, 1240, 1130, 1090, 1010, 835; nmr(CDCl₃, δ) 0.20(s, 9H, Si(CH₃)₃), 1.10(s, 3H, CH₃), 1.15(s, 3H, CH₃), 1.33(s, 3H, CH₃); m/e 226, 224, 188, 154, 117, 115, 95, 93, 73. An analytical sample was prepared by preparative gc at 140°, an amorphous solid (mp 31-35°).

**Anal. Calcd. for C₉H₁₂Cl₂Si:** C, 48.08; H, 8.02.
**Found:** C, 48.09; H, 8.12.

1,1-Dibromo-2,2,3-trimethyl-3-trimethylsilylcyclopropane (14).

Bromoform (25 g, 0.1 mol) was added dropwise with stirring to 2-methyl-3-trimethylsilyl-2-butene (10 g, 0.07 mol) and potassium t-butoxide (11 g, 0.1 mol) in t-butanol (110 ml) at 0°. The mixture was then stirred for 12 hr at room temperature, poured into water (1000 ml),
and extracted with pentane. The organic layer was dried with magnesium sulfate and the solvent removed under reduced pressure to leave crude 1,1-dibromo-2,2,3-trimethyl-3-trimethylsilylcyclopropane (14, 9.2 g, 42%). An analytical sample was prepared by vacuum distillation, 64-68°/0.3 mm; ir(film, cm⁻¹) 2950, 1440, 1390, 1240, 1140, 1070, 1000, 890, 830; nmr (CDCl₃, δ) 0.22(s, 9H, Si(CH₃)₃), 1.08(s, 3H, CH₃), 1.14(s, 3H, CH₃), 1.31(s, 3H, CH₃); m/e 316, 314, 312, 243, 241, 239, 162, 160, 149, 147, 73.


Found: C, 34.28; H, 5.88.

1-Chloro-2,3,3-trimethylcyclopropene (18).

Dry potassium fluoride (3 g) was added to 1,1-dichloro-2,2,3-trimethyl-3-trimethylsilylcyclopropane (2.25 g, 10 mmol) in dry dimethylsulfoxide (50 ml) and the mixture stirred 24 hr at room temperature. The mixture was poured into water (500 ml) and extracted with pentane. After drying the organic layer with magnesium sulfate, removal of the solvent left 1-chloro-2,3,3-trimethylcyclopropene (18, 710 mg, 61%), bp ~ 120°; ir
(film, cm$^{-1}$) 2900, 1440, 1350, 1240, 1100, 1010, 905, 770; nmr (CDCl$_3$, 6) 1.70(s, 6H, gem CH$_3$), 1.77(s, 3H, vinyl CH$_3$); exact mass: calcd. for C$_6$H$_9$Cl: 116.03927; found, 116.03958. An analytical sample was prepared by preparative gc at 155°.

**Anal.** Calcd. for C$_6$H$_9$Cl: C, 61.81; H, 7.73.

Found: C, 61.66; H, 7.78.

An alternate procedure for preparation of 18 involved use of 18-crown-6 ether (50 mg) with the same procedure, size, and workup as just described. The difference was that after 12 hr of stirring, a 980 mg (84%) yield of 1-chloro-2,3,3-trimethylcyclopropene (18) was obtained.

**1-Bromo-2,3,3-trimethylcyclopropene (19).**

A suspension of potassium fluoride (3 g) was stirred 24 hr with 1,1-dibromo-2,3,3-trimethyl-3-trimethylcyclopropane (3.14 g, 10 ml) in dimethylsulfoxide (50 ml). The mixture was poured into water (500 ml) and extracted with pentane. After drying the organic layer, removal of the solvent left 1-bromo-2,3,3-trimethylcyclopropene (19, 950 mg, 59%). An analytical sample was
obtained by preparative gc at 160°, ir(film, cm\(^{-1}\)) 2850, 1440, 1320, 1240, 1100, 1000, 895, 750; nmr (CDCl\(_3\), \(\delta\))

1.69(s, 6H, gem CH\(_3\)), 1.75(s, 3H, vinyl CH\(_3\)); exact mass: calcd. for C\(_6\)H\(_9\)Br: 159.9888; found, 159.9891.

Anal. Calcd. for C\(_6\)H\(_9\)Br: C, 44.78; H, 5.60.

Found: C, 44.84; H, 5.64.

Using the same procedure and size as just described, except for the addition of 18-crown-6 ether (50 mg) and stirring for 12 hr, gave a yield of 1.3 g (81%) of 1-bromo-2,3,3-trimethylcyclopropene, identical to an authentic sample.
REFERENCES


