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THE CHEMISTRY OF NAPHTHO[de]CYCLOBUTYL SYSTEMS

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

By
Peter John Card, B.S.

The Ohio State University
1976

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Department of Chemistry
To my Parents
ACKNOWLEDGMENTS

I would like to thank Dr. Harold Shechter for the suggestion of this research problem and his expert guidance in the preparation of this dissertation.

The financial support of The Ohio State University, The National Science Foundation, and the Procter and Gamble Company are gratefully acknowledged.
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The present research involves investigation of the chemistry of 1-bromo-1H-cyclobuta[de]naphthalene (I) and its utility as a precursor to 1-substituted-1H-cyclobuta[de]naphthalenes. The principle objectives of this study thus involve varied functionalizations of I at C(1) and exploration of the chemistry of these unique molecules.
HISTORICAL

Highly strained aromatic hydrocarbons have long been of intense interest to the organic chemist. The geometrical constraints and inherent strain in such molecules frequently cause them to undergo chemical reactions which are not observed in their higher homologs.

Naphthalenes bridged at the peri-positions by single atom moieties have been synthesized only recently. 1,8-Naphthalenediol (2) is reported to dehydrate to naphth[1,8-bc]oxete (3) at 300° (Equation 1);¹ this work cannot be repeated, however.²

\[ \text{HO} \quad \text{OH} \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{O} \quad \text{HO} \quad \\xrightarrow{300°} \quad \text{O} \quad \text{HO} \]


Photolysis of 1-isopropylideneaminonaphtho[1,8-de]triazine (1) yields 1-(2-propenyl)naphthalene (2); the desired product 1,1-dimethyl-1H-cyclobuta[de]naphthalene (6) is not observed (Equation 2).  

\[
\begin{align*}
\text{N} & \quad \text{N} & \quad \text{N} \\
\begin{array}{c}
\text{CH}_3 \\
\text{N} & \quad \text{N} & \quad \text{N} \\
\text{CH}_3
\end{array} & \quad \text{by} & \quad \text{CH}_3 \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\text{H}_3\text{C} & \quad \text{C} & \quad \text{CH}_2 \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N}
\end{align*}
\]


Preparation of 1H-cyclobuta[de]naphthalen-1-ylidenemethanone (7) via thermal or photochemical Wolff ring contraction of 2-diazoacenaphthenone (8) has failed (Equation 3).
Photolysis of 8 in electron poor solvents yields only polymeric products. Decompositions in aromatic or olefinic solvents results, however, in addition of α-oxocarbene 2 to the double bonds.

For example, photolysis of 8 in benzene gives spiro-compound 11 (84%, Equation 5) which isomerizes to 2-phenylacenaphthenone (12) in refluxing xylene.
Formation of carbene dimer 10 and norcaradiene 11 are doubtless reflections of the inability of 2 to undergo Wolff ring contraction because of the strain in the 1H-cyclobuta[de]naphthalene system.

Attempts to prepare naphtho[1,8-bc]azete (16) via thermolysis of naphtho[1,8-de]triazine (13) have been unsuccessful and result in formation of 1-aminonaphthalene (15, Equation 6).
The first reliable report of isolation of a single-atom peri-bridged naphthalene is that of Hoffman and Seiber. Upon irradiation through quartz naphtho[1,8-de]1,2,3-thiadiazine 1,1-dioxide (17) extrudes nitrogen to form naphtho[1,8-bc]thiete 1,1-dioxide (19, 25%) and disulfone (20, 3%) presumably through diradical (18) (Equation 7).
When heated above 185° sulfone 12 loses sulfur dioxide to give products which may be rationalized in terms of 1,8-dehydro-naphthalene (21, 1,8-naphthylene, Equation 8) as a reaction intermediate. Thus the 1,8-naphthylene (21) formed is trapped with dimethyl acetylenedicarboxylate to give 1,2-dicarbomethoxyacenaphthylene (22, 0.15%) and dimerizes to perylene (23, 0.4%).

Sulfone 12 rearranges at 300° (2 mm Hg) to naphtho[1,8-cd]-[1.2]oxathiol-5-oxide (24, 54%, Equation 9) but may be regenerated from 24 by treatment with acid.
The parent sulfide, naphtho[1,8-bc]thiete (26), has also been prepared by photolytic extrusion. Thus irradiation of


naphtho[1,8-cd]1,2 dithiole 1,1-dioxide (25) in benzene through pyrex results in evolution of sulfur dioxide and formation of 26 in 97% yield (Equation 10).

\[
\begin{align*}
\text{S} & \overset{0}{=} \text{hv} \\
\text{C}_6\text{H}_6 & \rightarrow \\
\text{25} & \rightarrow \\
\text{26} & + \text{SO}_2
\end{align*}
\]

(10)

The structure of 26 is consistent with its pmr and C\text{13} nmr spectra. Additional evidence for 26 is its oxidation by m-chloroperbenzoic acid to previously reported sulfone 19 via the intermediate sulfoxide 27 (Equation 11).

\[
\begin{align*}
\text{26} & \overset{\text{RCO}_2\text{H}}{\overset{70\%}{\rightarrow}} \text{27} \\
\text{27} & \overset{\text{RCO}_2\text{H}}{\overset{80\%}{\rightarrow}} \text{19}
\end{align*}
\]

(11)
Sulfide 26 and sulfone 19 readily undergo ring cleavage upon reactions with lithium aluminum hydride. Thus hydride reduction of 26 followed by methylation gives methyl 1-naphthyl sulfide (28, Equation 12) in 72% yield.

\[
\text{26} \quad \xrightarrow{1) \text{LiAlH}_4} \quad \xrightarrow{2) \text{NaOH, CH}_3\text{I}} \quad \text{28}
\]

Likewise, reduction of sulfone 19 and then methylation result in 28 (13%) and methyl 1-naphthyl sulfone (22, 65%); 1,1-dinaphthyl disulfide (30, 2%, Equation 13) is also formed as a minor product.
Reaction of 26 with methyl lithium proceeds via nucleophilic attack at sulfur to give methyl 1-naphthyl sulfide (28, Equation 14) as the major product; 8-methyl-1-naphthalenethiol is not observed.

\[ \text{26} \quad \text{CH}_3\text{Li} \rightarrow \quad \text{28} \]

(14)

The first examples of naphthalene bridged at the 1,8-positions by single carbon atom moieties were reported by Bailey and Shechter. Irradiation through pyrex of an ethereal suspension of the sodium salt of 8-bromo-1-naphthaldehyde p-tosylhydrazone (31) or 8-bromo-1-naphthyldiazomethane (32) in diethyl ether yields 1-bromo-\( \text{H-cyclobut[a]napthalene} \) (1, 44%) along with trans-bis-(8-bromo-1-naphthyl)ethylene (33, 15%, Equation 15).

The structure of \( \mathbf{1} \) is supported by its pmr and \( ^{13}\text{C} \) nmr spectra which are consistent with a symmetrical peri-substituted naphthalene.

Formation of \( \mathbf{1} \) from \( \mathbf{2} \) is postulated to proceed via photolytic loss of nitrogen to give carbene \( \mathbf{3} \), which reacts with the lone-pair electrons on bromine to form bromonium ylid \( \mathbf{3} \), which then collapses as in Equation 16.

\[
\begin{align*}
\mathbf{2} & \xrightarrow{\text{hv} - \text{N}_2} \mathbf{3} & \rightarrow \mathbf{1} \quad (16)
\end{align*}
\]

Bromide \( \mathbf{1} \) reacts with silver nitrate in aqueous dioxane at 60° to give 1-naphthaldehyde (36, 26%), \( 1-(1\text{H-cyclobuta[de]}\text{-naphthyl}) \text{nitrato} \) (37) and silver bromide (Equation 17). Aldehyde

\[
\begin{align*}
\text{H} & \xrightarrow{\text{Br}} \xrightarrow{\text{AgNO}_3, \text{H}_2\text{O}} 0 & \xrightarrow{\text{H}} \xrightarrow{\text{ONO}_2} \quad (17)
\end{align*}
\]

36 apparently arises by isomerization of the intermediate alcohol, 1-hydroxy-1\text{H-cyclobuta[de]}naphthalene (38, Equation 18).
Reactio

**Reaction of bromide \( l \) with magnesium and hydrolysis of the resulting Grignard reagent yields \( 1H \)-cyclobut[a]naphthalene** (Equation 19). On the basis of nmr evidence \( 32 \) appears to be essentially planar or a rapidly equilibrating puckered conformer.

Peri-bridged silicinaphthalenes have recently been synthesized via successive displacements on dialkyldichlorosilanes by 1,8-dilithionaphthalene.\(^\text{(10)}\) In this manner 1,8-dilithionaphthalene

\[ \text{Equation 19} \]

---


\( \text{(10)} \) reacts with dimethyldichlorosilane (\( \text{H}_3 \)) and diethyldichlorosilane (\( \text{H}_2 \)) to give 1,1-dimethylnaphtho[1,8-bc]silet \( (\text{H}_3, > 25\%) \) and 1,1-diethylnaphtho[1,8-bc]silet \( (\text{H}_4, > 43\%, \text{Equation 20}) \), respectively. Silet \( \text{H}_3 \) is unstable to air and moisture; hydrolysis
of $\text{LiCl}$ results in cleavage of the silicon bridge to give 1,1,3,3-tetramethyl-1,3-bis(1-naphthyl)disiloxane ($\text{45}$, Equation 21).

[Diagram showing reactions involving LiCl and ZCl₂]

1,8-Dilithionaphthalene ($\text{42}$) has also been used to prepare 1H-cyclobuta[de]naphthalene ($\text{39}$).\(^\text{(11)}\) Thus $\text{40}$

(11) L.S. Yang, private communication, The Ohio State University.

reacts with methylene chloride to form hydrocarbon $\text{39}$ (9\%) along with naphthalene (Equation 22). A better yield (19\%) of $\text{39}$

[Diagram showing reaction with CH₂Cl₂]

\(^{(11)}\)
may be obtained by reaction of 1,8-di(iodomagnesio)naphthalene (46) with methylene ditosylate (47, Equation 23).

\[ \text{Mg}_2\text{I}_2 + \text{CH}_2(\text{OSO}_2\text{C}_7\text{H}_7)_2 \rightarrow 2\text{H} + \text{naphthalene} \] (23)
RESULTS AND DISCUSSION

The chemistry and synthetic utility of 1-bromo-1H-cyclobuta[de]naphthalene (1) and its derivatives have presently been investigated.

The scheme employed for preparing 1 is a modification of the method of Bailey.\textsuperscript{12} Treatment of disodium 1,8-naphthalate (18)

\begin{align*}
(18) \text{R. J. Bailey, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio (1974).}
\end{align*}

with mercuric acetate in aqueous acetic acid followed by thermal decarboxylation gives almost quantitative yields of anhydro-8-hydroxymercuri-1-naphthoic acid (19, Equation 24).

\begin{equation}
\text{NaO}_{2}\text{C} \quad \text{CO}_{2}\text{Na} \quad \text{1) Hg(OAc)_{2}} \quad \text{2) } \Delta, -\text{CO}_{2} \quad \text{(24)}
\end{equation}

Bromination of naphthomercural 19 with tribromide ion in aqueous acetic acid yields 8-bromo-1-naphthoic acid (50, 75\%) which is converted by thionyl chloride to 8-bromo-1-naphthoyl chloride (51, 85\%) and thence to 8-bromo-1-naphthalenemethanol (52, 85\%) by
lithium aluminium hydride. Reduction of the acid chloride

allows for large scale preparation of 52 and offers a distinct
experimental advantage over the previous method which necessitates
the use of diazomethane. 8-Bromo-1-naphthaldehyde (53) was then
prepared by oxidation of 52 with N-chlorosuccinimide/dimethyl
sulfide/triethylamine in 73% yield which is a marked improvement
over the 41% previously reported. The increased yield of 53 was
achieved by lengthening the reaction time (see Experimental).
Aldehyde 53 was converted to 8-bromo-1-naphthaldehyde p-tosyl-
hydrazone (31) by acid catalyzed condensation with p-tosylhydrazide
(Scheme 1).

Irradiation of sodium 8-bromo-1-naphthyl p-tosylhydrazone
(31) or 8-bromo-1-naphthyl diazomethane (32) in ether yields
1-bromo-1H-cyclobuta[de]naphthalene (1, 32%) along with trans-bis-
(8-bromo-1-naphthyl)ethylene (33, 15%, Equation 25).
Scheme 1

49 \[\text{Br}_2, \text{KBr}\] \rightarrow 50 \[\text{BrCO}_2\text{H}\] \[\text{SOCl}_2\] \rightarrow 51 \[\text{BrCCl}_2\]

52 \[\text{LiAlH}_4, \text{Et}_2\text{O}\] \[1) \text{NCS, DMS}, 2) \text{TEA}\] \[\text{BrCH}_2\text{OH}\] \rightarrow 53

54 \[\text{H}_2\text{NNHSO}_2\text{C}_7\text{H}_7\] \rightarrow 55
Bromide 1 is probably formed from 8-bromo-1-naphthylmethylidene (32) via interaction of the carbenic center and the lone-pair electrons on bromine (see Equation 16) and then insertion (see Appendix). Attempts to capture carbene 32 by irradiation of 32 in methylenecyclohexane have failed.

The x-ray crystal structure of 1 has been determined by M. Gessner and G.G. Christoph.\(^{14}\) The bond distances and angles of 1 of interest are summarized in Table 1. Comparison of the
TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) OF INTEREST IN 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>1-bromo-1H-cyclobuta[de]naphthalene (1)</th>
<th>Naphthalene (54)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1a)-C(2)</td>
<td>1.356(6)</td>
<td>1.361(4)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.432(6)</td>
<td>1.421(4)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.381(6)</td>
<td>1.361(4)</td>
</tr>
<tr>
<td>C(4)-C(9)</td>
<td>1.420(7)</td>
<td>1.425(4)</td>
</tr>
<tr>
<td>C(9)-C(8)</td>
<td>1.382(6)</td>
<td>1.410(4)</td>
</tr>
<tr>
<td>C(1a)-C(8)</td>
<td>1.368(6)</td>
<td>1.435(4)</td>
</tr>
<tr>
<td>C(8)-C(1a)-C(2)</td>
<td>118.4(6)</td>
<td>120.2(2)</td>
</tr>
<tr>
<td>C(1a)-C(2)-C(3)</td>
<td>114.6(6)</td>
<td>120.5(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>124.4(6)</td>
<td>120.5(2)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(9)</td>
<td>120.2(6)</td>
<td>120.2(2)</td>
</tr>
<tr>
<td>C(4)-C(9)-C(8)</td>
<td>111.1(6)</td>
<td>119.2(2)</td>
</tr>
<tr>
<td>C(9)-C(8)-C(1a)</td>
<td>130.7(6)</td>
<td>119.2(2)</td>
</tr>
<tr>
<td>C(4)-C(9)-C(5)</td>
<td>137.7(6)</td>
<td>121.5(2)</td>
</tr>
<tr>
<td>C(1a)-C(8)-C(7a)</td>
<td>98.7(6)</td>
<td>121.5(2)</td>
</tr>
</tbody>
</table>

dimensions of 1 with naphthalene (54) reveals the changes which occur in the bonding parameters in the naphthalene system due to peri-bridging.
Bromide 1 is essentially planar (Figure 1). The bonds to the bromomethano bridge, which might be expected to be highly stretched, are only ca 0.03 Å longer than a normal carbon-carbon single bond and are similar to those in planar cyclobutanes. The strain in 1 is not concentrated solely in the C(1)-C(1a) and

Figure 1. X-Ray Structure of 1-Bromo-1H-cyclobuta[de]naphthalene (1).
C(1)-C(7a) bridge bonds, but rather is expressed by bond length and interbond angle distortions throughout the molecule. This finding accounts for the unexpected thermal stabilities of \( \text{I} \) and its derivatives.

Bridging the peri positions by the bromomethano moiety leads to compression of the portion of the naphthalene nucleus directly connected to the bridge and causes the opposite side of the molecule to expand. In particular, the C(1a)-C(8)-C(7a) angle is compressed to 99°, all of the bands to C(8) are substantially shorter than in naphthalene, and the C(4)-C(9)-C(5) angle is opened to 138°. The strain effects in \( \text{I} \) are similar to those reported recently for naphtho[1,8-bc]thiete 1,1-dioxide (19).^{15}


Bromide \( \text{I} \) reacts with magnesium in refluxing tetrahydrofuran and with n-butyllithium at -78° to form the corresponding organometallic derivatives \( \text{55} \) and \( \text{56} \) respectively (Equation 26).
The pmr spectrum of \( \text{55 (THF-}d_8 \text{)} \) exhibits a singlet at 3.95 \( \delta \) which corresponds to a 2.81 ppm upfield shift for the proton at C(1). The protons at C(2) and C(7) now appear at 6.65 \( \delta \), a net upfield shift of 0.53 ppm, while those at C(3) and C(4) are shifted ~ 0.4 ppm upfield. These observations are possibly indicative of slight ionic character in the carbon-magnesium bond with charge delocalization into the naphthalene nucleus.

Protonation of \( \text{55} \) produces 1H-cyclobuta[de]naphthalene (39, 100\%, Equation 27), bp 62-64° (0.24 mm), which is precipitable as its picrate, mp 151-153°. The proton and C\(^{13}\) nmr spectra of 39 show that the apical protons are equivalent, implying that the naphthalene ring of 39 is planar or undergoing rapid interconversion.
of nonplanar conformations. In an attempt to freeze-out any possible interconversions the system was cooled to \(-110^\circ\) and the nmr spectrum determined. However, even at \(-110^\circ\) the apical protons of 22 appear as a sharp singlet, and there is no evidence for an AB quartet. Therefore, if 22 undergoes rapid equilibrating puckered conformational change, the energy barrier to interconversion is very low.

A study was then made of generation of the carbanion by other methods. Base-catalyzed deuterium exchange of the apical protons of 22 occurs only under vigorous conditions. Neither potassium \(\text{t-butoxide}\) nor sodium dimsylate effect deprotonation of 22 at ambient temperatures as determined by nmr analysis. Deuteration is accomplished by heating 22 in sodium dimsylate/DMSO-\(d_6\) at \(75^\circ\) over an extended period of time, for instance, 22 is only 32% exchanged after 20 hr.

Competitive deuterium exchange studies were undertaken in order to determine the relative kinetic acidity of 22. The experiments were conducted by heating a solution of the hydrocarbon in sodium dimsylate/DMSO-\(d_6\) at \(75^\circ\) and monitoring the progress of exchange by nmr analysis. The extremely slow rate of deuterium exchange of 22 is clearly illustrated in Table 2. Thus acenaphthene (27) and diphenylmethane (58) undergo deuterium
TABLE 2
DEUTERIUM EXCHANGE (%)\textsuperscript{a} AT 75\textdegree

<table>
<thead>
<tr>
<th>Time</th>
<th>1H-Cyclobuta[de]naphthalene</th>
<th>Acenaphthene</th>
<th>Diphenylmethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min</td>
<td>--</td>
<td>--</td>
<td>89</td>
</tr>
<tr>
<td>0.5 hr</td>
<td>--</td>
<td>46.5</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>1.5</td>
<td>--</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>32</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>46</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>13 days</td>
<td>88</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values determined by nmr analysis

exchange faster than 32 by factors of at least 40 and 7200 respectively. The resistance of the dibenzylc protons of 37 to strong bases must be due to an inability of the naphthalene nucleus to delocalize negative charge at C(1) because of the excessive molecular strain implied in the possible resonance structures 52.
Carbanion formation from 32 is efficiently effected by treatment with t-butyllithium at 20-25°. Thus, addition of t-butyllithium to 32 in tetrahydrofuran, followed by hydrolysis with deuterium oxide gives 60 (76% yield) containing 47% deuterium at C(1) which corresponds to 94% carbanion formation (Equation 28).

\[
\begin{align*}
32 & \xrightarrow{1) \text{t-BuLi}} 60 \\
 & \xrightarrow{2) \text{D}_2\text{O}} 
\end{align*}
\]

(28)

Functionalization of C(1) may be accomplished through Grignard reagent 55. Reaction of 55 with trimethylchlorosilane gives 1-trimethylsilyl-1H-cyclobuta[de]naphthalene (61, 66%, Equation 29) and 32.

\[
\begin{align*}
55 & \xrightarrow{(\text{CH}_3)_3\text{SiCl}} 61 
\end{align*}
\]

(29)

The structure of 61 is consistent with its pmr and C\text{\textsuperscript{13}} nmr spectra which are indicative of a symmetrically bridged naphthalene derivative.
The strain in 1H-cyclobuta[de]naphthalene and its derivatives is evidenced by the ease of cleavage of the cyclobutyl ring by catalytic hydrogenation. Thus hydrogenation of 39 in methanol over 10% palladium on carbon at atmospheric pressure yields 1-methyl-naphthalene (62, R = H; 94%, Equation 30). Similarly, 1-trimethylsilyl-1H-cyclobuta[de]naphthalene (61, R = Si(CH₃)₃) is reduced at 40 psi to 1-[(trimethylsilyl)methyl]naphthalene (62, R = Si(CH₃)₃; 80%, Equation 30). The structure of 62 is established by combustion analysis and spectral properties including nmr absorptions at δ 0.05 (s, 9H, -Si(CH₃)₃), 2.62 (s, 2H, methylene), and 7.1-8.1 (m, 7H, aromatic).

![Diagram](image)

Reactions of Grignard reagent 55 with carbon dioxide and subsequent acidification produce 1H-cyclobuta[de]naphthalene-1-carboxylic acid (64, 30%, Equation 31). Supportive evidence for the structure of 64 are infrared absorptions (cm⁻¹) at 3350-2750 (O-H stretching) and 1730 (carboxyl); nmr absorption at δ 5.97
(s, 1H, bridge proton); exact mass and combustion analysis. Carboxylic acid 64 is converted by diazomethane to methyl 1H-cyclobuta[de]naphthalene-1-carboxylate (65, 97.5%, Equation 31) whose structure is indicated by its infrared and nmr spectral properties.

Grignard reagent 55 reacts with methyl iodide in refluxing tetrahydrofuran to give a 4:1 mixture of 1-methyl-1H-cyclobuta[de]-naphthalene (66) and 32 respectively (Equation 32).

Efficient separation of 66 from 32 could not be achieved either by vapor phase or high pressure liquid chromatography. The two components were identified by comparison of their gas chromatographic retention times and the nmr spectrum of the mixture to those of authentic samples prepared by an independent route as subsequently described.

Functionalization at C(1) may also be achieved via nucleophilic displacement. Thus reaction of bromide 1 with lithium aluminum
hydride or sodium bis(2-methoxyethoxy)aluminum hydride in ether gives hydrocarbon $39$ quantitatively (Equation 33).

\[
\text{Br} \quad \text{LiAlH}_4 \quad \text{H} \\
1 \quad 29
\]

(33)

Analogously, refluxing an acetonitrile solution of $1$, potassium iodide, and a trace amount of 18-crown-6 for 60 hr results in formation of 1-iodo-1H-cyclobuta[de]naphthalene ($67$, 91\%, Equation 34).

\[
\text{I} \quad \text{KI,CH}_3\text{CN} \quad 18\text{-crown-6} \quad \text{H} \\
1 \quad 67
\]

(34)

Iodide $67$ is of proper combustion analysis and its structure is consistent with its pmr and seven line $^{13}$C nmr spectra.

Treatment of bromide $1$ with sodium thiophenoxide in refluxing absolute ethanol produces 1-thiophenoxy-1H-cyclobuta[de]naphthalene ($68$, 85\%, Equation 35).

\[
\text{H} \quad \text{NaS} \phi \quad \text{HO}_3\text{C}-\text{C}_6\text{H}_4\text{-Cl-M} \quad \text{H} \\
1 \quad 68 \quad 69
\]

(35)
The structure of sulfide 68 is established by its combustion analysis and spectral properties including nmr absorptions at δ 6.30 (s, 1H, bridge), and 6.87-7.45 (m, 11H, aromatic); and a C\textsuperscript{13} nmr spectrum which consists of eleven lines. Sulfide 68 is readily oxidized by m-chloroperbenzoic acid to 1-(phenylsulfonyl)-1H-cyclobuta[de]naphthalene (69, 89%, Equation 35). Supportive data for the structure of 69 include -SO\textsubscript{2}− infrared absorptions at 1380 and 1140 cm\textsuperscript{-1}, nmr absorptions at δ 6.4 (s, 1H, bridge), and 7.1-7.91 (m, 11H, aromatic), and combustion analysis.

Sodium azide converts bromide 1 efficiently in hexamethylphosphoramide to 1-azido-1H-cyclobuta[de]naphthalene (70, 94%, Equation 36), a colorless solid which decomposes slowly in the presence of light or upon storage at room temperature. Azide 70 may be kept, however, indefinitely at -20°. The structure of 70 is in accord with its spectral properties including infrared absorptions at 2120 and 1320 cm\textsuperscript{-1} (N\textsubscript{3}); nmr absorption at δ 6.17 (broads, 1H, bridge); mass spectral absorption, m/e = 181, for its parent ion; and a C\textsuperscript{13} nmr spectrum which consists of seven lines.
Thermolysis of azide $\text{70}$ at 150° for 0.5 hr in anhydrous hexamethylphosphoramide gives 1-cyanonaphthalene ($\text{71}$, 67%) as the only isolated product (Equation 37). Photolysis of $\text{70}$ in pentane

$$\text{70} \xrightarrow{150^\circ \text{HMPA}} \text{71} + \text{N}_2$$

yields 1-cyanonaphthalene $\text{71}$ (13.5%) along with intractables. No benz[c,d]indole ($\text{72}$) or products derived therefrom are observed in either experiment. Interestingly enough, $\text{72}$ is an unreported molecule and may itself represent a fascinating research project.

A number of mechanisms may be envisioned for formation of 1-cyanonaphthalene from $\text{70}$ (Scheme 2). The decompositions are presumed to involve thermal or photochemical loss of nitrogen from azide $\text{70}$ to give nitrene $\text{73}$ which then rearranges by paths a or b to form $\text{71}$. Path a involves intramolecular ring opening to the indicated dipolar species $\text{74}$, proton transfer would then give the observed product. Path b proceeds from nitrene $\text{73}$ via hydrogen
Scheme 2

\[ \text{Scheme 2} \]

\[ \begin{align*}
\text{To} & \xrightarrow{\Delta \text{ or } hv} \text{12} \\
\text{12} & \xrightarrow{a} \text{14} \rightarrow \text{12} \\
\text{12} & \xrightarrow{b} \text{15} \rightarrow \text{16} \\
\end{align*} \]
migration to nitrogen with resultant formation of imine $\text{7}_2$, ring cleavage to diradical $\text{7}_6$, and subsequent hydrogen atom migration produces $\text{7}_1$.

1-Cyano-1$H$-cyclobuta[de]naphthalene ($\text{7}_7$) is potentially useful as a precursor to various functionalized derivatives of 1$H$-cyclobuta[de]naphthalene. However, attempts to prepare $\text{7}_7$ under a variety of conditions (see Experimental) via nucleophilic substitution upon $\text{1}$ were unsuccessful and led only to intractable material. These results are puzzling in light of the facile displacement of bromide by nucleophiles and the stability of the 1$H$-cyclobuta[de]naphthalene system.

Reaction of bromide $\text{1}$ with sodium methoxide in refluxing methanol and aqueous work-up of the product results in 1-methoxy-1$H$-cyclobuta[de]naphthalene ($\text{7}_8$, 16.5%) and a 61:39 mixture of 1-naphthaldehyde ($\text{3}_6$) and 1-naphthaldehyde dimethyl acetal ($\text{7}_9$, Equation 38). Methoxy derivative $\text{7}_8$ was identified by its spectral properties including infrared absorptions at 1200 and 1120 cm$^{-1}$ (C-O); nmr absorptions at $\delta$ 3.42 (s, 3H, OCH$_3$), 6.64 (s, 1H, bridge), 7.2 (d of d, 2H, ortho), and 7.44-7.7 (m, 4H, meta and para); and mass spectral absorption, m/e = 170, for its parent ion.
Assignments of the additional reaction products as 1-naphthaldehyde and 1-naphthaldehyde dimethyl acetal are based on the infrared and nmr spectra of the mixture. Treatment of the mixture of 36 and 72 with 2,4-dinitrophenylhydrazine also produces 1-naphthaldehyde 2,4-dinitrophenylhydrazone (60%, mp 250-253°, lit. 16 254°). Sodium methoxide and 1 in hexamethylphosphoramide at 75° for 40 hr followed by hydrolytic work-up yields 1-naphthaldehyde (36, 60%) along with unreacted 1 (25%).


Formation of 36 and 72 may be rationalized on the basis of attack by methoxide at C(1) on 78 with concomitant ring cleavage.
and subsequent protonation (Equation 39) to produce 72 which hydrolyzes to 36 on work-up.

Displacement of 1 by amines also results in ring opened products. Thus bromide 1 reacts with aniline in hexamethylphosphoramide at 90° for 7 days to give 1-naphthaldehyde (36, 26%) along with recovered bromide 1 (36.5%) after hydrolytic work-up (Equation 40).

Various mechanisms rationalize formation of the 1-naphthaldehyde. Initial attack by aniline on bromide 1 might produce 1-(phenylamino)-1H-cyclobuta[de]naphthalene (82) which may proceed to 36 as in Scheme 3. Path a involves attack by aniline on 80 to form aminal 81 which hydrolyzes to 1-naphthaldehyde, and is analogous to the mechanism postulated for the reaction of 78 and methoxide ion. Path b does not require further attack by aniline but involves a ring opening reaction through an iminium ion to anil 82 and subsequent hydrolysis to 36.
Scheme 3

1 → \( \cdot \cdot \cdot \) \( \cdot \cdot \cdot \) H Br

\[ \text{\( \cdot \cdot \cdot \) \( \cdot \cdot \cdot \) H} \]

\[ \text{H \( \cdot \cdot \cdot \) H} \]

80 \( \rightarrow \) \( \cdot \cdot \cdot \) \( \cdot \cdot \cdot \) H N\( \Phi \)

\[ \text{H \( \cdot \cdot \cdot \) H} \]

81 \( \rightarrow \) \( \cdot \cdot \cdot \) \( \cdot \cdot \cdot \) H CH(NH\( \Phi \))\( _2 \)

\[ \text{H \( \cdot \cdot \cdot \) H} \]

82 \( \rightarrow \) \( \cdot \cdot \cdot \) \( \cdot \cdot \cdot \) H CH=N\( \Phi \)

\[ \text{H \( \cdot \cdot \cdot \) H} \]

\[ \text{H} \]

\( \text{81} \)

\( \text{82} \)

\( \text{H} \)

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Treatment of 1 with piperidine at 20-25° for 24 hr forms piperidine hydrobromide and 1-naphthaldehyde (36, 64%, Equation 41) after hydrolysis. Formation of 36 may be explained by mechanistic pathways analogous to those in Scheme 3.

\[
1 \xrightarrow{1) C_{5}H_{11}N} \xrightarrow{2) H_{2}O} 36
\]  

(41)

Isolation of ring opened products from displacements of bromide 1 with methoxide, aniline, and piperidine gives evidence for considerable strain in the sigma bonds of the cyclobutyl moiety. Such ring opening processes may limit use of nucleophilic substitution for synthesis of 1H-cyclobuta[de]naphthalene derivatives.

Functionalization at C(1) may also be achieved via displacement of bromide 1 with triphenylphosphine. Thus bromide 1 reacts with triphenylphosphine in refluxing xylene to give 1-triphenylphosphonium-1H-cyclobuta[de]naphthalene bromide (85) in 96.5% yield (Equation 42).

\[
1 \xrightarrow{\Delta, \text{xylene}} \xrightarrow{\Phi_{3}P} 85
\]  

(42)
The structure of $\mathbf{33}$ is established by its combustion analysis and its nmr absorptions at $\delta 7.23$ (m, 2H, ortho protons on naphthalene), and $7.5 - 7.98$ (m, 20H).

Reaction of phosphonium salt $\mathbf{33}$ with sodium dimsylate in dimethyl sulfoxide and then acetone produces 1-isopropylidene-$1H$-cyclobuta[de]naphthalene (34, 48%, mp 64.5-66.5°) and $1H$-cyclobuta[de]naphthalene (39, 32%, Equation 43). Treatment of $\mathbf{33}$ with $n$-butyllithium in ether and subsequent reaction with acetone also gives olefin $\mathbf{35}$ (36%) and bridged hydrocarbon $\mathbf{39}$ (44%). The assignment of $\mathbf{33}$ is consistent with its combustion analysis and its spectral properties including nmr absorptions at $\delta 2.02$ (s, 6H, -CH$_3$), 7.04 (d of d, 2H, ortho), and 7.43 (m, 4H, meta and para); a C$^{13}$ nmr spectrum consisting of nine lines; and mass spectral absorption, m/e = 180, for its parent ion.

Formation of $\mathbf{39}$ is rationalized by nucleophilic attack of sodium dimsylate or n-butyllithium at phosphorous with displacement of the $1H$-cyclobuta[de]naphthalen-1-yl carbanion (56), subsequent protonation then gives $\mathbf{39}$ (Equation 44).
If 52 arises as a result of nucleophilic attack by the base at phosphorus, then the use of a stronger, less nucleophilic base should increase the yield of olefin 55. Thus addition of t-butyl-lithium to a suspension of 52 in tetrahydrofuran at 0°, and subsequent treatment of the resulting ylid with acetone gives 55 in 80% yield. No 1H-cyclobuta[de]naphthalene (32) is observed.

Use of t-butyllithium to form the highly reactive ylid 8b provides an extremely useful synthetic entry into 1H-cyclobuta[de]-naphthalenes containing an sp² hybridized carbon at C(1). Thus ylid 8b condenses with acetaldehyde at room temperature to give 1-ethylidene-1H-cyclobuta[de]naphthalene (86, 84.5%, Equation 45),

\[
\begin{align*}
&\text{CH}_3\text{CH} = \text{CH} = \text{C} = \text{C} = \text{O} \\
\rightarrow \\
&\text{H} - \text{CH} = \text{C} = \text{C} = \text{CH}_3
\end{align*}
\]  

bp 70-75° (0.2 mm). The structure of 86 is established by combustion analysis and spectral properties including infrared absorption at 1700 cm⁻¹ (c=c, olefinic); nmr absorptions at δ 2.0 (d, 3H, J=6.5 Hz, -CH₃), 5.8 (q, 1H, J=6.5 Hz, olefinic proton), 6.95-7.27 (m,
2H, ortho), and 7.34-7.59 (m, 4H, meta and para); and mass spectral absorption at m/e = 166, for its parent ion.

Ylid $\mathbf{84}$ reacts with benzaldehyde at 20-25° to form 1-benzylidene-1H-cyclobuta[de]naphthalene (87, 85%, Equation 46), a white solid,

\[ \mathbf{84} \xrightarrow{\mathbf{\phi}} \mathbf{87} \]

mp 54-56°. Olefin 87 is identified by its mass spectrum (m/e = 228), proper combustion analysis, and nmr absorptions at $\delta$ 6.74 (s, 1H, olefinic) and 7.06 - 7.77 (m, 11H, aromatic).

When ylid $\mathbf{84}$ and paraformaldehyde is refluxed in tetrahydrofuran for 2 hr 1-methylene-1H-cyclobuta[de]naphthalene (88, 85%, Equation 47) is obtained as a colorless liquid, bp 70° (0.45 mm). The

\[ \mathbf{84} \xrightarrow{\text{(CH}_2\text{O)}_3} \Delta, \text{THF} \]

structure of 88 is confirmed by its combustion analysis and spectral properties including infrared absorption at 1700 cm$^{-1}$ (C=C, olefinic); nmr absorptions at $\delta$ 5.45 (s, 2H, olefinic), 7.16 (d of d, 2H, ortho), and 7.52 (m, 4H, meta and para); and mass spectral absorption at m/e = 152, for its parent ion. In addition, 88 displays an eight line
C^{13} nmr spectrum which requires a symmetrically bridged naphthalene derivative.

Ultraviolet absorption spectra of 85, 86, 87, and 88 are compared with 1H-cyclobuta[de]naphthalene (32) in Table 3.

TABLE 3
ULTRAVIOLET ABSORPTION SPECTRA OF 85, 86, 87, 88, and 32

<table>
<thead>
<tr>
<th>Compound</th>
<th>EtOH λ_{max} nm(ε)</th>
<th>nm(ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>88</td>
<td>323(1,381) 311(1,214)</td>
<td>257(12,456)\textsuperscript{a} 221(62,500)</td>
</tr>
<tr>
<td>86</td>
<td>321(932) 309(1,619)</td>
<td>258(16,621)\textsuperscript{a} 218(74,324)</td>
</tr>
<tr>
<td>85</td>
<td>309(1,856) 262(17,900)\textsuperscript{a}</td>
<td>222(81,700)</td>
</tr>
<tr>
<td>87</td>
<td>322(13,410) 297(22,988) 277(22,050)\textsuperscript{a}</td>
<td>222(79,510)</td>
</tr>
<tr>
<td>32</td>
<td>312(341) 272(4,640)\textsuperscript{a}</td>
<td>224(69,500)</td>
</tr>
</tbody>
</table>

The shift to shorter wavelength and the increase in the transverse\textsuperscript{a} bands in the olefins when compared to 32 are perhaps indicative of some electronic interaction between the carbon-carbon double bond and the naphthalene moiety.

A study was then made of reduction of 1-alkylidene-1H-cyclobuta[de]naphthalenes. Hydrogenation of 1-isopropylidene-1H-cyclobuta[de]naphthalene (85) in methanol at atmospheric pressure over 10% palladium on carbon results in saturation of the double
bond and reductive cleavage of the cyclobutyl ring to give
1-isobutynaphthalene (89, > 93\%, Equation 48). No 1-isopropyl-1H-
cyclobuta[de]naphthalene is observed.

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{CH}_3 \\
\text{H}_2/\text{Pd-C} \\
\text{MeOH}
\end{array} \quad \xrightarrow{\text{Diimide reduction}} \quad \begin{array}{c}
\text{H} \\
\text{CH}_2\text{CH} (\text{CH}_3)_2
\end{array}
\]

Diimide reduction\(^{17}\) of 88 in methanol yields 1-methyl-1H-
cyclobuta[de]naphthalene (66, 61\%, Equation 49) along with initial
88 (5\%). Olefin 88 is efficiently separated from 66 via

---

82, 410 (1960).

---

\[
\begin{array}{c}
\text{H} \\
\text{CH}_3
\end{array} \quad \xrightarrow{\text{N}_2\text{H}_2} \quad \begin{array}{c}
\text{H} \\
\text{CH}_3
\end{array}
\]

epoxidation and column chromatography. The structure of 66 is
consistent with its combustion analysis, nmr absorptions at \(\delta 1.67\)
(d, 3H, J = 7 Hz, -CH\(_3\)), 5.15 (q, 1H, J = 7Hz, bridge), 6.88 (d of d,
2H, ortho), and 7.1-7.5 (m, 4H, meta and para), and an eight line
\(\text{C}^{13}\) nmr spectrum.
Under conditions for reduction of 88 by diimide, 1-ethylidene-1H-cyclobuta[de]naphthalene (86) is unchanged. The reluctance of 86 to undergo diimide reduction is presumably due to the steric effect of the methyl group.

The pyrolytic behavior of various 1H-cyclobuta[de]naphthalenes was then investigated. Passage of 1-methyl-1H-cyclobuta[de]naphthalene (66) through a hot tube at $456^\circ$ (0.1 mm) gives 1-vinyl-naphthalene (92) in 79.5% yield (Equation 50). 1-Vinylnaphthalene (92)

$$66 \xrightarrow{456^\circ, \text{0.1 mm}} 21 \rightarrow 90$$

is identified by comparison of its infrared spectrum with that of a standard sample, and by its nmr absorptions at $\delta 5.28-5.92$ (m, 3H, olefinic) and $7.17-8.17$ (m, 7H, aromatic). Thermal rearrangement of 66 probably occurs via homolytic ring cleavage to form 1,4-di-radical 21 and subsequent hydrogen transfer through a six-membered cyclic transition state to give 90 (Equation 50).

Thermal rearrangements of 1-methylene-1H-cyclobuta[de]-naphthalene (89), 1-ethylidene-1H-cyclobuta[de]naphthalene (86), and 1-benzylidene-1H-cyclobuta[de]naphthalene (87) yield acetylenic naphthalenes. Thus 88 isomerizes at $550^\circ$ (0.1 mm) to 1-ethynyl-naphthalene (93, 73%, Equation 51). Identification of 93 is based
Formation of 92 is rationalized by homolytic ring cleavage of 88 and then hydrogen transfer to C(8) in 1,4-diradical 92 via a 6-membered cyclic process.

At 550° (0.1 mm) 86 pyrolyzes to 1-(1-propynyl)naphthalene (24, 44%, Equation 52; 56% 86 is recovered) and 87 rearranges at 650° (0.1 mm) to 1-(phenylethynyl)naphthalene (25, 66%, Equation 53). The structure of 25 is assigned on the basis of its chemical
origin and spectral properties including nmr absorptions at 
$\delta$ 7.19-7.9 (m, 11H, aromatic), and 8.4 (m, 1H, peri proton). The 
appearance of a one proton multiplet at 8.4 $\delta$ is indicative of the 
product structure as it arises from a deshielding of the proton at 
C(8) by the carbon-carbon triple bond.

The thermal chemistry of $85$ differs from that of the above 
olefins. Passing $85$ at 0.1 mm through a tube heated above 700° 
gives a mixture (54%) which consists of a major and a minor (10%, 
nmr analysis) component (Equation 54) which could not be separated

$$
\begin{align*}
&\text{H}_3\text{C} - \text{CH}_3 \\
&\xrightarrow{\text{700°, 0.1 mm}} \\
&\text{H}_3\text{C} - \text{CH}_3
\end{align*}
$$

by standard techniques. The major component was tentatively 
identified as 1,2-dimethylacenaphthylene (27, 90% relative yield) 
by comparison of literature data (20) with the observed spectral

properties; ir absorption at 1620 cm\(^{-1}\) (C = C), and nmr absorptions at 6 2.2 (s, -CH\(_3\)), and 6.95 - 7.7 (m, aromatic). The minor product is as yet unidentified. Formation of \(\text{27}\) from \(\text{25}\) cannot be explained by the previous mechanism for olefin rearrangement but probably occurs via migration of a bridging sigma bond to the terminal olefinic carbon giving carbene \(\text{26}\) (Equation 54), which undergoes methyl migration producing \(\text{27}\).

The photolytic behavior of various 1\(H\)-cyclobuta[de]naphthalenes was then investigated. Irradiation of \(\text{26}\) in methanol or pentane for 8 hr through Vycor produces dark amorphous material which could not be identified along with recovered olefin.

Photolysis of the parent hydrocarbon \(\text{32}\) in pentane for 6 hr in quartz results in 74\% recovery of \(\text{32}\) and a yellow-brown intractable precipitate that could not be characterized. 1,4-Diradical \(\text{28}\) may possibly be generated upon photochemical excitation of \(\text{32}\). Attempted trapping of \(\text{28}\) via irradiation of \(\text{32}\) in isopropyl alcohol produces

\[
\text{CH}_2
\]

a dark precipitate along with recovered \(\text{32}\) (80\%). Neither 1-methylnaphthalene nor isopropoxy products were detected either by nmr or gas chromatography.
Addition of hydrogen bromide to 88 provides for further functionalization at C(1). Reaction of 88 in methylene chloride with 1 equivalent of gaseous hydrogen bromide at \(-26^\circ\) for 24 hr gives 1-bromo-1-methyl-1H-cyclobuta[de]naphthalene (99, 78%, Equation 55) as a colorless solid (mp 90-92.5\(^\circ\)), and recovered 88 (19\%). The structure of 99 is consistent with its combustion analysis and spectral properties including nmr absorptions at \(\delta\) 2.47 (s, 3H, \(-\text{CH}_3\)), 7.08 (d of d, 2H, ortho) and 7.27-7.58 (m, 4H, meta and para); and a C\(^{13}\) nmr spectrum consisting of eight lines.

The formation of 99 via Markownikoff addition implies the intermediacy of the 1-methyl-1H-cyclobuta[de]naphthalen-1-yl carbonium ion (100) which necessarily possesses greater stability than the alternative primary carbonium ion. Generation of 100 is
interesting since the internal angle at C(1) must be significantly smaller than the 120° angle favored by trigonal planar intermediates.

Treatment of 86 in chloroform at 0° with m-chloroperbenzoic acid and storage at -10° for 24 hr results in epoxidation to form 3'-methylspiro[1H-cyclobuta[d]naphthalene-1,2'-oxirane] (101, 85%, Equation 56). The structure of 101 is established by combustion analysis and its spectral properties.

\[
\begin{align*}
86 & \xrightarrow{\text{MCPBA}} CHCl_3, -10^\circ \rightarrow 101 \\
\end{align*}
\]

Epoxide 101 reacts with lithium aluminum hydride to give \(\alpha\)-ethyl-1-naphthalenemethanol (102, 95%, Equation 57).

\[
\begin{align*}
101 & \xrightarrow{1) \text{LiAlH}_4, \text{Et}_2\text{O}} 102 \\
 & \xrightarrow{2) \text{H}_3\text{O}^+} \\
\end{align*}
\]

The structure of 102 is consistent with its spectral properties including infrared absorption at 3380 cm\(^{-1}\) (OH) and nmr absorptions at \(\delta\) 0.85 (*, 3H, -CH\(_3\)), 1.8 (m, 2H, -CH\(_2\)-), 2.58 (broad s, 1H, OH), 5.1 (z, 1H, benzylic), and 7.08-7.97 (m, 7H, aromatic). Alcohol 102 was further identified via independent synthesis from 1-naphthaldehyde (36) and ethylmagnesium bromide.
Formation of 102 obviously occurs via hydride attack at C(5) of 101 to give bridged alkoxide 103, which undergoes ring opening to produce ketone 104. Reduction with lithium aluminum hydride and subsequent protonation converts ketone 104 into alcohol 102 (Equation 58).

\[
\begin{align*}
101 & \xrightarrow{\text{LiAlH}_4} 103 \\
103 & \xrightarrow{\text{LiAlH}_4, \text{H}_2\text{O}} 102 \\
\end{align*}
\]

Boron trifluoride etherate effects rearrangement of epoxide 101 to a mixture of 2-methylenacenaphthenone (105, 69%), and 1H-cyclobuta[de]naphthalen-1-yl methyl ketone (106, 11%), along with several minor components which were not identified (Equation 59).

\[
\begin{align*}
101 & \xrightarrow{\text{BF}_3} 105 + 106 \\
\end{align*}
\]

2-Methylenacenaphthenone is identified by its chemical origin and its spectral characteristics including ir absorption at 1720 cm\(^{-1}\) (C=O),
and nmr absorptions at $\delta$ 1.49 (d, 3H, -CH$_3$), 3.55 (q, 1H, benzylic) and 7.27-8.08 (m, 6H, aromatic), which are in agreement with published data.$^{20}$

The structure of methyl ketone $^{106}$ is assigned from its combustion analysis, spectral properties including infrared absorption at 1720 cm$^{-1}$ (C=O), and nmr absorptions at $\delta$ 2.3 (s, 3H, -CH$_3$), 5.88 (s, 1H, bridge), 7.09-7.27 (d of d, 2H, ortho), and 7.34-7.76 (m, 4H, aromatic), and its chemical origin. Additional proof for $^{106}$ was obtained by independent synthesis (21%) from Grignard reagent $^{55}$ and acetyl chloride.

Ketones $^{105}$ and $^{106}$ most probably arise from paths a and b respectively (Equation 60), and the observed 7:1 product ratio is possibly an indication of the relative stabilities of carbonium ions $^{107}$ and $^{108}$.

\[
\begin{align*}
101 & \xrightarrow{BF_3} 107 & \rightarrow 105 \\
101 & \xrightarrow{BF_3} 108 & \rightarrow 106
\end{align*}
\]
1H-Cyclobuta[de]naphthalene-1-one (108) is of interest as a source of 1,8-naphthalyne (21) and various functionalized derivatives of 1H-cyclobuta[de]naphthalene. Attempts to prepare 108 by oxidative cleavage of 85 with osmium tetroxide-sodium periodate leads to intractable products. Ozonolysis of 85 in ethyl acetate and decomposition of the resulting ozonide with dimethyl sulfide however gives ketone 108 (71%, Equation 61; mp 51.5-53.5°) along with recovered 85 (29%).


\[
\begin{align*}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{CH}_3 \\
\end{array} & \xrightarrow{1) \text{O}_3} \\
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array} & \xrightarrow{2) (\text{CH}_3)\text{S}} \\
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\end{array}
\end{align*}
\]

(61)

Combustion analysis, mass spectroscopy (m/e = 154), infrared absorption at 1775 cm\(^{-1}\) (C=O, four membered ring), nmr absorptions at \(\delta\) 7.34 (d of d, 2H, ortho), and 7.5-7.9 (m, 4H, meta and para), and a C\(^{13}\) nmr spectrum consisting of seven lines confirms the structure of 108.
Ketone 108 exhibits a C^{13} chemical shift of 178.2 ppm for C(1). Strained alicyclic ketones typically display carbonyl C^{13} shifts in the range 208-215 ppm; thus the cyclobutanone C^{13} carbonyl absorption shift is 208.2 ppm. The upfield shift (178.2 ppm) of C(1) in 108 is probably the result of a combination of both strain and π conjugative effects.


Attempts to prepare ketone 108 via photodecarbonylation ofacenaphthenequinone (109) failed (Equation 62). Thus irradiation

\[
\begin{align*}
109 & \xrightarrow{h\nu} 108 \\
\;
\end{align*}
\]

of 109 for 67 hr in hexane results in 88% recovery of 109.

Ketone 108 is also preparable, albeit in low yield, from 1-chloro-1-thiophenoxy-1H-cyclobuta[de]naphthalene (110), as obtained (92.5%, Equation 63; mp 74-75°) from 1-thiophenoxy-1H-cyclobuta[de]naphthalene (68) and N-chlorosuccinimide in refluxing carbon tetrachloride. The assignment of 110 is consistent with its
nmr spectrum which contains only aromatic resonances, and its $^{13}$

Attempts to hydrolyze $\text{110}$ to $\text{108}$ (according to the methods of
Paquette and Snow, private communication, The Ohio State University)
with aqueous sodium carbonate, aqueous mercuric chloride/cadmium
carbonate, and chloramine-T in aqueous methanol resulted in minor
yields (<5 - 12%) of ketone $\text{108}$ (Equation 63). Chloride $\text{110}$ is
quite resistant to hydrolysis and the principal material from these
experiments is recovered $\text{110}$. The stability of $\text{110}$ to hydrolysis
is presumably a reflection of the reluctance of C(1) to become $sp^2$
hybridized.

The strain in ketone $\text{108}$ is also revealed by its rapid ring-
opening reactions. Thus $\text{108}$ is converted by anhydrous methanol at

$\text{20-25}^\circ$ in one hour to methyl 1-naphthoate ($\text{112}$, 69%, Equation 64).
Formation of $\text{112}$ from $\text{108}$ is rationalized on the basis of addition
of methanol across the carbonyl group to form hemiketal $\text{111}$,
which then undergoes ring opening with proton transfer to give 112 (Equation 64).

Base-catalyzed hydrolysis of 108 also results in ring opening. Thus, treatment of 108 with potassium hydroxide in hexamethylphosphortriamide at room temperature results in potassium 1-naphthoate (113, 88%, Equation 65).

\[
108 \xrightarrow{\text{KOH}} 113
\]

A study was then made of addition of nitrogen nucleophiles to 108. Thus refluxing a mixture of ketone 108 and aniline in benzene produces 1-naphthanilide (115, 80.5%, Equation 66). The formation of anilide 115 from 108 probably occurs via attack at C(1) to give hemiaminal 114, which then rearranges to 115.

Attempts to prepare carbonyl derivatives of ketone 108 also leads to ring opened products. Thus 108 reacts with 2,4-dinitrophenylhydrazine in ethanol or in concentrated sulfuric acid to
give 1-naphthoic acid 2,4-dinitrophosphylhydrazide (116, Equation 67, mp 275-278° w/dec). The structure of 116 is assigned from its amide carbonyl absorption at 1640 cm\(^{-1}\); mass spectral absorption at m/e = 352 for its parent ion; and sulfuric acid catalyzed hydrolysis to 1-naphthoic acid.

Ketone 108 is potentially useful for preparing bridged olefinic derivatives via the Wittig reaction. However, reaction of 108 with triphenylphosphoniummethylide also leads to ring cleavage. Thus addition of 108 to triphenylphosphoniummethylide in tetrahydrofuran results in ring opening and subsequent proton transfer to give ylid 117 (Equation 68). The structure of 117 is established.
by hydrolysis to 1-acetonaphthalene (118, 17.5%, Equation 68). No 1-methylene-1H-cyclobuta[de]naphthalene (88) was observed.

1,8-Naphthalyne (1,8-dehyronaphthalene, 21) is of particular interest because the proximity and orientation of the peri-dehydro-orbitals could lead to some overlap and stabilization similar to that in ortho-benzylene.24 When 21 is generated by lead tetracetae oxidation of 1-aminonaphtho[1,8-de]triazine (119) in benzene, both fluoronethene (120) and 1-phenynaphthalene (121) are isolated as reaction products (Equation 69).25 Formation of 120

is rationalized via 1,2 addition to benzene to give 9,14-dihydrofluoranthene which is oxidized further. 1-Phenynaphthalene is presumably formed via hydrogen abstraction from benzene and radical recombination.

Naphthalyne 21 reacts with olefins and acetylenes via 1,2-addition to yield acenaphthene and acenaphthylene derivatives respectively. Thus 21 adds to dimethyl acetylenedicarboxylate to give 1,2-dicarbomethoxyacenaphthylene (22) in 30% yield (Equation 70).

\[
21 + \text{dimethyl acetylenedicarboxylate} \rightarrow 22
\]

Decarbonylation of ketone 108 has been presently investigated as a source of 1,8-naphthalyne (Equation 71). Thermolysis of 108 at 180 to 350°C and photolysis of 108 in dimethyl acetylenedicarboxylate results however in amorphous materials and recovery of small amounts of initial 108. No 1,2-dicarbomethoxyacenaphthylene (Equation 72) is observed. Also thermolysis of 108 in refluxing cumene produces
intractables along with initial ketone $^{108}$ (33%). Naphthalene and 1-naphthaldehyde ($^{76}$), which might arise via hydrogen abstraction by 21 and 122 respectively, are not found. Decomposition of $^{108}$ requires further detailed study.

An investigation was then made of the chemistry and utility of the $^{1H}$-cyclobuta[de]naphthalen-1-yl carbonium ion ($^{123}$).

Generation of $^{123}$ should be retarded because of the small internal bond angle available to C(1). Indeed $^{108}$ in ethanolic silver nitrate must be warmed before a precipitate of silver bromide is formed; 9-bromofluorene gives an instantaneous silver bromide test with ethanolic silver nitrate.

Bromide 1 reacts with silver acetate in hexamethylphosphor-triamide at 75° to give 1-acetoxy-$^{1H}$-cyclobuta[de]naphthalene ($^{124}$, 86%, Equation 73) and recovered bromide (1, 7.3%). Acetate $^{124}$,
a colorless oil, is precipitable as its picrate (mp 113-115°).

The structure of 12^ is consistent with the combustion analysis of
its picrate and its spectral properties including infrared
absorption at 1740 cm⁻¹ (C=O, ester), nmr absorptions at 6 2.05
(s, 3H, OOCCH₃), 7.0-7.28 (m, 3H, ortho and bridge protons), and
7.34-7.67 (m, 4H, meta and para), and a C¹³ nmr spectrum which
consists of nine lines. Formation of 12b from bromide 1 probably
occurs by silver ion assisted solvolysis of 1 to form carbonium
ion 123 and subsequent capture by acetate ion.

Acetate 12^ is of interest as a precursor to 1-hydroxy-1H-
cyclobuta[de]naphthalene (38, Equation 74). Hydrolysates of 12^
(36, 70%, Equation 74) as the only isolated product, similar results are obtained in the varied hydrolyses. Formation of 36 from 124 is easily envisioned as a ring opening reaction of alcohol 38.

Reduction of 124 with lithium aluminum hydride in ether results in formation of 1-naphtalénemethanol (126, 63%) along with recovered acetate 124 (35%, Equation 75). Formation of

\[
124 \xrightarrow{\text{LiAlH}_4, \text{Et}_2\text{O}} 125
\]

\[
1 \xrightarrow{\text{LiAlH}_4} 125 \xrightarrow{\text{H}_2\text{O}} 126
\]

alcohol 126 along with recovery of unreacted acetate 124 is suggestive of facile ring opening of the initially formed alkoxide 125 to give 36, which undergoes rapid reduction by lithium aluminum hydride to 126.

Acid-catalyzed hydrolysis of 124 also leads to ring opened products. Thus refluxing 124 in anhydrous methanol containing catalytic quantities of concentrated hydrochloric acid produces a
68:32 mixture of 1-naphthaldehyde (36) and 1-naphthaldehyde dimethyl acetal (72, Equation 76) in 82% overall yield.

\[
\begin{align*}
124 & \xrightarrow{\text{HCl}} \text{CH(OCH}_3)_2 + 36 \\
\text{CH}_2\text{OH} & \begin{array}{c}
\text{72}
\end{array}
\end{align*}
\]

Bromide 1 reacts with silver acetate in acetic acid at 75° (Equation 77) to give 1-naphthaldehyde (36, 29%) and α,α-diacetoxy-1-methylnaphthalene (127, 55%) along with unreacted bromide (1, 16%).

\[
\begin{align*}
1 & \xrightarrow{\text{AgOCOC}_2\text{H}_3, \text{HOAc}, 75^\circ} \text{CH(OOCH}_3)_2 + 36 \\
\text{72} & \begin{array}{c}
\text{127}
\end{array}
\end{align*}
\]

The structure of 127 is established by its combustion analysis and spectral properties including infrared absorptions at 1760 (C=O, ester) and 1740 cm\(^{-1}\) (C=O, ester), and nmr absorptions at \(\delta\) 2.09 (s, 6H, OOCCH\(_3\)), 7.32-7.88 (m, 6H, aromatic), and 8.1-8.25 (m, 2H, peri proton and benzylic proton).

Reaction of 1 with silver acetate and acetic acid is rationalized on the basis of initial solvolysis of 1 and capture by acetate ion to yield acetate 124, and then silver ion catalyzed
ring opening of \( \text{126} \) to carbonium ion \( \text{128} \) which reacts with acetic acid to give \( \text{127} \). Aldehyde \( \text{36} \) is presumably formed via hydrolysis of diacetate \( \text{127} \).

\[
\text{128} \xrightarrow{\text{AgOAc, HOAc, 75°}} \text{127}
\]

The sensitivity of the 1H-cyclobuta[de]naphthalene system to silver ion is revealed further by the reaction of hydrocarbon \( \text{32} \) with silver acetate in acetic acid at 75° to form 1-naphthalene-methanol acetate (\( \text{129}, 84.5\% \), Equation 79), as evidenced by infrared absorption at 1750 cm\(^{-1}\) (C=O, ester); and nmr absorptions at 6 2.03 (S, 3H, OCOCH\(_3\)), 5.53 (s, 2H, benzylic), and 7.34-8.09 (m, 7H, aromatic).

\[
\text{32} \xrightarrow{\text{AgOAc, HOAc, 75°}} \text{129}
\]

Bromide \( \text{1} \) in hexamethylphosphorotriamide reacts with silver tosylate at 75° to give 1H-cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (\( \text{130}, 45\% \)) along with 1-naphthaldehyde (\( \text{36}, 12.7\% \)) and
recovered bromide \( 1 \) (25%, Equation 80). Combustion analysis, mass spectroscopy \((m/e = 310)\), infrared absorptions at 1180 and 1175 cm\(^{-1}\)

\[
\begin{align*}
\text{H} & \quad \text{O}_{2}\text{C}_7\text{H}_7 \\
1 & \xrightarrow{\text{AgOTs, HMPA, } 75^\circ} \quad + \text{36} \\
\end{align*}
\]

(80)

\( 130 \)

\( 80_2 \); nmr absorptions at \( \delta 2.43 \) (s, 3H, -CH\(_3\)) and 6.85=8.05 (m, 11H, aromatic and bridge protons), and a \( c^{13} \) nmr spectrum consisting of twelve lines confirm the structure of \( 130 \).

A study was then made of the acetylation of \( 1^H\)-cyclobuta[de]-naphthalen-1-yl \( p \)-toluenesulfonate at \( 75^\circ \). Heating tosylate \( 130 \) in acetic acid at \( 75^\circ \) for 5 days results in formation of acetate \( 124 \) (15%) and 1-naphthaldehyde \( 36 \) (3%) along with an 82% recovery of unreacted \( 130 \) (Equation 81). Acetylation at \( 75^\circ \) over a period of

\[
\begin{align*}
\text{H} & \quad \text{OAc} \\
130 & \xrightarrow{\text{HOAc, } 75^\circ} \quad \rightarrow \text{36} \\
\end{align*}
\]

(81)

27 days yields \( 36 \) (82%) and a 12.5% recovery of \( 130 \). Formation of 1-naphthaldehyde \( 36 \) in the acetylation of \( 130 \) may be rationalized on the basis of initial formation of acetate \( 124 \) which then undergoes
acid catalyzed ring opening and subsequent hydrolysis to give $36$. In an independent experiment, acetate $12^4$ was heated in acetic acid at $75^\circ$ for 25 days to give, after hydrolytic work-up, a 4:1 mixture of $12^4$ and $36$.

It is of interest that tosylate $130$ solvolyzes only 18% in 5 days at $75^\circ$, whereas at $25^\circ$ acetic acid converts 9-fluorenyl tosylate rapidly (53% in 5.2 min)$^{26}$ and benzhydryl tosylate (too fast to measure)$^{27}$ to their acetates. The extremely slow rate of


\[ \text{(27) G.W. Corwell, A. Ledwith, and D.G. Morris, ibid, 700 (1967).} \]

solvolysis of tosylate $130$ is no doubt an indication of the instability of carbonium ion $12^3$ due to the small C(1a)-C(1)-C(7a) bond angle available to it.

Generation of the 1H-cyclobuta[de]naphthalen-1-yl radical $131$ from bromide $1$ and hydrocarbon $39$ was then studied. Reaction of $39$ and benzoyl peroxide with N-bromosuccinimide thus results in bromide $1$ (40%) and recovery of $39$ (56%, Equation 82). Formation of $1$ is postulated to proceed through the intermediacy of radical $131$. 
Photolytic cleavage of the carbon-bromine bond in 1 also results in radical 131. Irradiation of 1 in cumene through quartz produces 32 (60%) presumably via hydrogen abstraction from cumene by radical 131.

Bridging the peri positions of naphthalene with the bromomethano moiety as in 1 affects expansion of the opposite side of the molecule. In particular, the C(4)-C(9)-C(5) angle is opened to 138° and the H(4)-H(5) distance increases (0.5 Å) to 2.94 Å. Because of the distortions placed upon the naphthalene nucleus by single-atom peri-bridging, it was of interest to determine whether 5-(6-bromoacenaphthyl)methyldiene (132) will undergo bridging to give 1-bromo-4,5-dimethylene-1H-cyclobuta[de]naphthalene (134, Equation 83). The dimethylene bridge in 132 causes widening of the
C(5)-C(10)-C(6) angle, thus making formation of bromonium ylid 133 and its subsequent collapse to $133^\frac{1}{2}$ more difficult. Also, bromide $133^\frac{1}{2}$ is of interest in that it is a strained analog of bromide 1 and represents a new carbon skeletal system.

5-(6-Bromoacenaphthenyl)diazomethane (135), the envisioned precursor of carbene 132, was synthesized from acenaphthene (57) via a scheme analogous to that used for 1. Thus reaction of 57

with N,N-dimethylcarbamoyl chloride (2 equiv) and hydrolysis of the resulting diamide with concentrated hydrochloric acid produces acenaphthene-5,6-dicarboxylic acid (136, 51%, Equation 84).  

![Diagram](image)

\[ \text{27} \xrightarrow{0} \text{135} \xrightarrow{1} \text{136} \]

(84)

Reaction of the disodium salt of diacid 136 with mercuric acetate in aqueous acetic acid, followed by thermal decarboxylation results in loss of carbon dioxide and formation of anhydro-6-hydroxymercuri-5-acenaphthenoic acid (137, 99%, Equation 85).

\[
136 \xrightarrow{1) \text{NaOH}} \xrightarrow{2) \text{Hg(OAc)}_2} \Delta \rightarrow 137
\]

Bromination of 137 with tribromide ion in acetic acid gives 6-bromo-5-acenaphthenecarboxylic acid\(^{29}\) (138, 81%), which is converted by ethereal diazomethane to methyl 6-bromo-5-acenaphthenecarboxylate (139, 91%). It is of note that thionyl chloride and oxaloyl chloride react with acid 138 to produce 6-bromo-5-acenaphthenoyl chloride only in yields less than 30%. Diisobutylaluminum hydride fails to effect reduction of 139 to 6-bromo-5-acenaphthenemethanol (140) but does reduce methyl 8-bromo-1-naphthoate to 8-bromo-1-naphthalenemethanol (52).\(^{12}\) These observations suggest that the carboxyl group in the 6-bromo-5-acenaphthenyl system is even more hindered than its 8-bromo-1-naphthyl analog. Reduction of 139 with lithium aluminum hydride

---

Scheme 4

137 \[\text{NaBr,Br}_2,\text{HOAc}\] $\rightarrow$ 138

139 \[\text{CH}_2\text{N}_2\] $\rightarrow$

139 \[\text{LiAlH}_4\] $\rightarrow$ 140

141 \[1)\text{NCS, DMS}, 2)\text{TEA}\] $\rightarrow$ 142

142 \[\text{C}_7\text{H}_7\text{SO}_2\text{NNH}_2,\text{EtOH}\] $\rightarrow$ 143
in ether results in a 95:5 mixture of 6-bromo-5-acenaphthene-
methanol (140) and 5-acenaphthenemethanol (141) respectively.

\[
\text{CH}_2\text{OH}
\]

\textbf{141}

Oxidation of 140 via N-chlorosuccinimide/dimethyl sulfide/
triethylamine produces 6-bromo-5-acenaphthenecarboxaldehyde (142,
55%) which is converted by p-toluenesulfonylhydrazide in ethanol
to 6-bromo-5-acenaphthenecarboxaldehyde p-tosylhydrazone (143) in
69% yield (Scheme 4).

Photolysis of an ethereal suspension of the sodium salt of
6-bromo-5-acenaphthenecarboxaldehyde p-tosylhydrazone (144) and
thermolysis of 144 in refluxing chlorobenzene results however in
amorphous materials. No 1-bromo-4,5-dimethylene-1H-cyclobuta[de]-
naphthalene (154, Equation 86) is observed. The inability to

\[
\begin{align*}
\text{Br} & & \text{CH=NNSO}_2\text{C}_7\text{H}_7 \\
\text{Na}^{+} & & \text{CH}_2\text{OH}
\end{align*}
\]

\textbf{144} \quad \xrightarrow{\Delta \text{ or } h_v} \quad \textbf{154} \quad (86)

isolate bromide 13b in the above decompositions possibly suggests
that in 132 the bromine atom and the carbenic center are separated
by a distance that is too large to allow bridging.
Recent study\textsuperscript{30} of irradiation of 2-diazoacenaphthenone (8) in solid argon matrix at low temperature and analysis of the infrared absorption of the product indicate that 1\textsubscript{H}-cyclobuta[de]naphtalen-1-ylidenemethane (7) is formed via Wolff ring contraction (Equation 87). In the present investigation,

\begin{equation}
\text{8} \xrightarrow{hv - N_2} \text{2} \rightarrow \text{7} \tag{87}
\end{equation}

photolysis of 8 in methanol has been studied in attempts to generate 7 and its conversion to methyl 1\textsubscript{H}-cyclobuta[de]naphtalen-1-yl carboxylate (65, Equation 88). Irradiation of 2-diazoacenaphthenone (8)\textsuperscript{31} in methanol at 20-25\degree, methanol at -78\degree, and 1:1

\begin{equation}
\text{7} + \text{CH}_3\text{OH} \rightarrow \text{H} \xrightarrow{\text{COCH}_3} \tag{88}
\end{equation}

\textsuperscript{(30)} O.L. Chapman, private communication, The University of California at Los Angeles.

methylenecly chloride/methanol at -78° results in loss of nitrogen and formation of an orange mixture of many products (tlc analysis) but which does not contain $65$ as evidenced by vpc analysis. The mass spectrum of the mixture exhibits absorption at m/e = 198 which corresponds to the mass of $65$, but unfortunately its fragmentation pattern is not consistent with that of $65$. The absorption at m/e = 198 may possibly be assigned to 2-methoxyace-
naphthenone (145) which results from insertion of carbene 2 across the O-H in methanol (Equation 89). The inability to isolate $65$

\[ \text{2} \xrightarrow{\text{CH}_3\text{OH}} \text{145} \]

in the above photolyses is no doubt a reflection of the inability of 2 to undergo Wolff ring contraction due to the strain in the 1H-cyclobuta[de]naphthalene system.
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 a Perkin Elmer, Model 137 or 457 recording spectrophotometer. All spectra were calibrated against a polystyrene absorption peak at 1601 cm⁻¹.

Proton Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra were obtained using Varian Associates nuclear magnetic resonance spectrometers, Models A-60, A-60A and HA-100, and Bruker HX-90. Chemical shifts were measured in ppm downfield from tetramethylsilane.

C¹³ Nuclear Magnetic Resonance Spectra. C¹³ nuclear magnetic resonance spectra were obtained using a Bruker Model HX-90 spectrometer, operating at 22.625 MHz. Chemical shifts were measured in ppm from tetramethylsilane.

Gas Chromatography. Gas chromatography was performed using a Wilkins Aerograph, Model A-90-P3 with a thermal conductivity detector.
Ultraviolet Spectra. Ultraviolet spectra were obtained with a Cary, Model 14 recording spectrophotometer.

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

Anhydro-8-hydroxymercuri-l-naphthoic Acid (49)

Two methods of preparation of 49 were employed; method I is superior and was used extensively in the present study.

Method I. 1,8-Naphthalic anhydride (49.5 g, 0.25 mol) was suspended in aqueous sodium hydroxide (35 g, 0.875 mol in 1500 ml water) and refluxed until all solid material had dissolved. Mercuric acetate (87.5 g, 0.275 mol) dissolved in water (250 ml) and glacial acetic acid (50 ml) was added to the sodium 1,8-naphthalate solution. After the mixture had been refluxed ~30 min, additional 75 ml of acetic acid 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-l-naphthoic acid was 90.0 g (97%).

Method II. 1,8-Naphthalic anhydride (39.6 g, 0.20 mol) was dissolved in aqueous sodium hydroxide (24.0 g, 0.60 mol in 1200 ml water) and filtered while hot. Mercuric acetate (70.0 g, 0.22 mol) dissolved in water (160 ml) and glacial acetic acid (48 ml) was added to the sodium 1,8-naphthalate solution. The mercuric
1,8-naphthalate was filtered, washed with distilled water and
dried in vacuo at 80° for 18 hr. The solid mercuric 1,8-naphthalate
was ground to a fine powder and slurried with powdered soft glass
(1 g) in hexamethylphosphorotriamide (400 ml). The slurry was
heated at 140° until gas evolution ceased, ~30 min. The slurry
was cooled to room temperature, poured into water (2200 ml), and
filtered. The tan solid was dissolved in aqueous sodium hydroxide
(16.0 g, 0.40 mol in 500 ml water) and filtered. Carbon dioxide
was bubbled through the stirred filtrate until the solution was
neutral to pH paper. The tan precipitate was filtered, washed with
water, and dried in vacuo at 80° for 18 hr. The yield of anhydro-
8-hydroxymercuri-l-naphthoic anhydride was 47.9 g (65%).

8-Bromo-l-naphthoic Acid (50)

Anhydro-8-hydroxymercuri-l-naphthoic acid (93.0 g, 0.25 mol)
was suspended in a solution of glacial acetic acid (380 ml) and
water (60 ml) in a 24 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 (170.0 g, 1.66 mol) in water (310 ml) and bromine
(41.7 g, 14.3 ml, 0.26 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
slowly heated to 100° and poured into a stirred mixture of ice (625 g) and water (625 ml). 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-l-naphthoic acid was 45.5 g (73%), mp 174-175°, lit. 12 175-176°; 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-l-naphthoyl Chloride (51).

8-Bromo-l-naphthoic acid (100.4 g, 0.4 mol) and thiocyanium chloride (248.0 g, 150 ml, 2.1 mol) were refluxed under nitrogen for 3 hr. The excess thiocyan chloride was removed under reduced pressure and the residue was recrystallized from hexane. The yield of 8-bromo-l-naphthoyl chloride was 89.9 g (84%), mp 66-68°, lit. 13 67-68°; ir (kBr, cm⁻¹) 1760 (acyl C=O).

8-Bromo-l-naphthyl Alcohol (52).

Lithium aluminum hydride (4.37 g, 0.115 mol) was suspended in anhydrous ethyl ether (115 ml) in a 1l 3-necked round bottom flask, fitted with a condenser, an addition funnel, and a mechanical stirrer. A solution of 8-bromo-l-naphthoyl chloride (38.3 g, 0.142 mol) in ethyl ether (450 ml) was added at a rate that just maintained a gentle reflux. After addition was complete, the
mixture was refluxed for 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 magnesium sulfate. The solvent was removed under reduced pressure and the white crystalline solid was recrystallized from cyclohexane. The yield of 8-bromo-1-naphthyl alcohol was 28.4 g (85%); mp 86-88°, lit.12 86-87°; ir (mull, cm⁻¹) 3500-3000 (OH), 1610, 1500, 1070, 890, 812, 762 (aromatic); nmr (CDCl₃, δ) 2.57 (broad s, 1H, CH₂OH), 5.50 (broad s, 2H, CH₃OH), 6.86-7.80 (m, 6H, aromatic).

8-Bromo-1-naphthaldehyde (53).

N-chlorosuccinimide (80.0 g, 0.6 mol) was dissolved in toluene (2500 ml) in a 5 l 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°. 8-Bromo-1-naphthyl alcohol (70.8 g, 0.3 mol) was added to toluene (500 ml), warmed to effect solution, and added to the chilled N-chlorosuccinimide-dimethyl sulfide complex. The mixture was stirred for 2.5 hr at -25°. Trimethylamine (45.0 g, 50 ml, 0.45 mol) was added and the mixture was allowed to warm to room temperature overnight and then poured into ethyl ether (6000 ml) and
filtered to remove the succinimide. The solution was concentrated to 200 ml, poured into ether, and filtered. The ethereal solution was extracted with 1N hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, and dried over magnesium sulfate. The solvents were removed under reduced pressure and the residue was recrystallized from ethanol. The yield of 8-bromo-1-naphthaldehyde was 51.0 g (75%); mp 87-88°, lit 89-90°; ir (mull, cm⁻¹) 1660 (aldehyde C=O), 1600, 1550, 1490, 826, 792, 750 (aromatic); nmr (CDCl₃, δ) 7.12-8.02 (m, 6H, aromatic), 11.31 (s, 1H, CHO).

8-Bromo-1-naphthaldehyde p-Tosylhydrazone (31).

8-Bromo-1-naphthaldehyde p-tosylhydrazone was prepared according to the method of R.J. Bailey in 85-90% yield from 8-bromo-1-naphthaldehyde, mp 193-195° with decomposition; ir (KBr, cm⁻¹) 3200 (NH), 1600, 1490, 1450, 940, 895, 812, 754 (aromatic), 1440, 1150 (SO₂); mass spectrum m/e 402, 404 (M⁺).

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

8-Bromo-1-naphthaldehyde p-tosylhydrazone (40.2 g, 0.1 mol) was slurried in dry dichloromethane (450 ml). Excess sodium hydride was washed with pentane and added in several portions to the p-tosylhydrazone slurry until hydrogen evolution ceased. The resulting solution was filtered through glass wool and evaporated...
to dryness. The sodium 8-bromo-1-naphthaldehyde p-tosylhydrazone was slurried in anhydrous ethyl ether (2300 ml) and irradiated for 17 hr with a 450 W 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 (45 g) and separated into two main fractions by column chromatography using distilled petroleum ether (bp 30-60°) as eluent. The products isolated were:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (1), 8.15 g (37.2%), recrystallized from ethanol, mp 102-104°, lit\textsuperscript{12} 102-104°; ir (KBr, cm\textsuperscript{-1}) 1600, 1460, 1145, 1005, 980, 820, 785, 775, 680 (aromatic); nmr (CDCl\textsubscript{3}, \delta) 6.76 (s, 1H, bridge), 7.18 (d of d, 2H, J=5 and 2Hz, ortho), 7.30-7.63 (m, 4H, meta and para).

2) trans-bis(8-bromo-1-naphthyl)ethylene (32), 4.8 g (11.1%), recrystallized from chloroform, mp 201-203°, lit\textsuperscript{12} 203-204°; nmr (CDCl\textsubscript{3}, \delta) 6.0-8.0 (m).

8-Bromo-1-naphthyldiazomethane (32).

8-Bromo-1-naphthaldehyde p-tosylhydrazone (1.0 g, 2.5 mmol) was mixed with 1,1,3,3-tetramethylguanidine\textsuperscript{32} (20 ml) and heated

upon a steam bath for 15 min. The resultant deep red solution was added to a slurry of ice and water and extracted with cold pentane. The organic layer was separated and treated with several small pieces of Dry Ice to precipitate any remaining tetramethyl-guanidine as its insoluble carbonate. The solution was then dried, filtered, and the pentane removed in vacuo to yield 8-bromo-1-naphthyldiazomethane (32) as a reddish-orange solid (0.29 g, 46%). Purification of 32 was effected by recrystallization from pentane at -78°C; mp 59-61°C; ir (CHCl₃, cm⁻¹) 2080 (C=N₂), 1550, 1450, 1380, 1100, 815, 795 (aromatic). Exact mass: calcd. 245.9795; found, 245.9799.

**Photolysis of 8-Bromo-1-naphthyldiazomethane (32) in Methylene-cyclohexane.**

A solution of 8-bromo-1-naphthyldiazomethane (60 mg, 0.24 mmol) in methylenecyclohexane (3 ml) was degassed with nitrogen and placed in a septum sealed pyrex photolysis tube. The mixture was irradiated with a 1000 W lamp (through a filtering system which eliminated wavelengths below 3400 Å) until the diazo absorption band at 2060 cm⁻¹ was absent in the infrared spectrum. The mixture was concentrated under reduced pressure to a dark brown oil. Nmr analysis of the crude product revealed it to be only 1-bromo-1H-cyclobuta[de]naphthalene (1) as evidenced by absorptions at δ 6.76 (s, 1H, bridge), 7.18 (d of d, 2H, ortho), and 7.3-7.68 (m, 4H, meta and para).
1H-Cyclobuta[de]naphthalene (39).

1-Bromo-1H-cyclobuta[de]naphthalene (4.4 g, 20 mmol) was dissolved in anhydrous ethyl ether (50 ml). Red-al (20 ml, a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene) in ethyl ether (30 ml) was added to the mixture at a rate that just maintained gentle reflux and the solution was then refluxed overnight. The mixture was cooled to room temperature and hydrolyzed with saturated sodium sulfate. The ethereal layer was extracted with water and saturated sodium chloride, dried, and concentrated to yield 1H-cyclobuta[de]naphthalene as a colorless oil (2.75 g, 98%). Purification via vacuum distillation produced pure hydrocarbon; 2.21 g (79%), bp 62-65° (0.24 mm). The product, on the basis of its nmr, ir, and vpc analysis (10 ft x ¼ in, 12.5% QP-1 on chromasorb W, isothermal at 150°, retention time ~ 5.5 min), was identical to an authentic sample prepared by Bailey.12

1H-Cyclobuta[de]naphthalene Picate.

1H-Cyclobuta[de]naphthalene (440 mg, 2 mmol) in hot ethanol (10 ml) was added to a solution of picric acid (460 mg, 2 mmol) in hot ethanol (10 ml) and the resulting mixture was allowed to cool to room temperature. The 1H-cyclobuta[de]naphthalene picate, a yellow solid which precipitated in quantitative yield, was washed with cold ethanol and after repeated recrystallization from ethyl ether at -78° gave the derivative as fine bright yellow needles, mp 151-153°.
Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Lithium Aluminum Deuteride.

1-Bromo-1H-cyclobuta[de]naphthalene (219 mg, 1.0 mmol) in anhydrous ethyl ether (5 ml) was slowly added to a suspension of lithium aluminum deuteride (42.0 mg, 1 mmol) in anhydrous ethyl ether (5 ml), and the mixture was refluxed under nitrogen for 96 hr. The mixture was cooled to room temperature, hydrolyzed by addition of saturated aqueous sodium sulfate, poured into water and extracted with ether. The organic layer was dried over magnesium sulfate, poured into water and extracted with ether. The organic layer was dried over magnesium sulfate and concentrated to yield 101 mg of a yellow oil. Analysis of the nmr spectrum revealed that 72% deuteride displacement had taken place. A pure sample of 1-deutero-1H-cyclobuta[de]naphthalene was obtained by vpc under the conditions used for 32; nmr (CDCl₃, δ) 4.80 (s, 1H, bridge), 7.1 (d of d, 2H, J = 5 and 2Hz), 7.25-7.65 (m, 4H).

Exact mass: calcd. 141.0688; found 141.0690.

Low Temperature NMR Spectrum of 1H-Cyclobuta[de]naphthalene (32).

A vpc purified sample of 1H-cyclobuta[de]naphthalene (35 mg, 0.25 mmol) dissolved in anhydrous carbon disulfide containing 1% TMS was sealed in an nmr tube under vacuum. The nmr spectrum
obtained at ambient temperature exhibited the characteristic bridge singlet at 4.8 δ. The probe was cooled to -110° as determined via a thermocouple and a spectrum was obtained. The low-temperature spectrum also exhibited only a singlet at 4.8 δ with no evidence for an AB quartet, 7.1 (d of d, 2H, ortho), and 7.25-7.65 (m, 4H, meta and para).

Reaction of 1H-Cyclobuta[de]naphthalene (39) with Potassium t-Butoxide in t-Butanol-d.

1H-Cyclobuta[de]naphthalene (39, 35 mg, 0.25 mmol) was dissolved in t-butanol-d (0.6 ml) and treated with a small amount of potassium t-butoxide (sublimed). The mixture was tumbled in an nmr tube for 12 hr after which nmr analysis revealed that no exchange had taken place. An additional amount of potassium t-butoxide was added and the solution tumbled for 10 hr. After a total of 22 hr no change in the nmr spectrum of starting hydrocarbon 39 was observed.

Reaction of 1H-Cyclobuta[de]naphthalene (39) with Sodium Dimsylate-d₅ in Dimethyl Sulfoxide-d₆ at Room Temperature.

Sodium dimsylate-d₅ in dimethyl sulfoxide-d₆ (prepared by treating dimethyl sulfoxide-d₆ with sodium hydride and heating on a water bath) was added to a solution of 1H-cyclobuta[de]naphthalene(39) in dimethyl sulfoxide-d₆ and the mixture was tumbled for 24 hr. No exchange was detected in the nmr spectrum after this time, the hydrocarbon remained unchanged.
When the sodium dimyslate was added to a solution of fluorene in dimethyl sulfoxide-$d_8$ the mixture rapidly turned deep red and its nmr spectrum revealed that 100% exchange had taken place.

Relative Rates of Deuterium Exchange of $^{1}H$-Cyclobuta[de]naphthalene (39), Acenaphthene (57), and Diphenylmethane (58).

A solution of the hydrocarbon in dimethyl sulfoxide-$d_8$ (~ 0.6M) containing sodium dimyslate-$d_8$ (0.08M) was heated at 75° and the progress of the reaction monitored by nmr analysis (see Table 2). exact mass: calcd. for C$_{11}$H$_5$D$_6$ 142.0751; found 142.0753.

Reaction of $^{1}H$-Cyclobuta[de]naphthalene (39) with $t$-Butyllithium in Tetrahydrofuran.

$t$-Butyllithium (1.6 mmol) in hexane was added to a solution of $^{1}H$-cyclobuta[de]naphthalene (52.5 mg, 0.375 mmol) in anhydrous tetrahydrofuran (5 ml) at room temperature. The mixture was stirred for 1 hr and quenched by the addition of deuterium oxide. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting colorless oil (40 mg, 76%) was a 94:6 mixture of 1-deutero-$^{1}H$-cyclobuta[de]naphthalene (60) and $^{1}H$-cyclobuta[de]naphthalene respectively (nmr analysis).

NMR Spectrum of $^{1}H$-Cyclobuta[de]naphthalenemagnesium Bromide (55).

1-Bromo-$^{1}H$-cyclobuta[de]naphthalene (1, 219 mg, 1 mmol) in anhydrous tetrahydrofuran-$d_8$ was added to sublimed magnesium
(25 mg, 1 mmol) and the mixture was refluxed for 2 hr. After cooling to room temperature, a 0.5 ml aliquot was removed and sealed in a dry nmr tube under reduced pressure. The nmr spectrum of at ambient temperature exhibited nmr absorptions at \( \delta 3.95 \) (s, 1H, bridge proton), \( 6.65 \) (m, 2H, ortho), and \( 7.0 \) (m, 4H, meta and para).

1-Trimethylsilyl-1H-cyclobuta[de]naphthalene (61).

1-Bromo-1H-cyclobuta[de]naphthalene (1, 4.38 g, 20 mmol) in anhydrous tetrahydrofuran (75 ml) was added to sublimed magnesium (0.53 g, 22 mmol) and the mixture was refluxed 12 hr. A solution of chlorotrimethylsilane (6.9 g, 5.0 ml, 64 mmol) in tetrahydrofuran (25 ml) was added and the mixture refluxed 48 hr. The solution was allowed to cool to room temperature and hydrolyzed by addition of saturated aqueous ammonium chloride. The layers were separated and the organic portion was washed with 10% hydrochloric acid and saturated aqueous sodium chloride, dried, and concentrated to give 3.1 g of an oily brown residue. The residue was distilled to yield a mixture (2.8 g) of 1-trimethylsilyl-1H-cyclobuta[de]naphthalene (61) and 1H-cyclobuta[de]naphthalene (39), bp 95-101° (1.15 mm).

Separation and isolation of the products by vpc (10 ft x \( \frac{1}{4} \) in, 5% SE-50 on chromasorb \( \gamma \), isothermal at 150°) gave:

1) 1-Trimethylsilyl-1H-cyclobuta[de]naphthalene (61), 66% as a semi-solid; ir (neat, cm\(^{-1}\)) 3030 (aromatic C-H), 2950
(aliphatic C-H), 1240 (C-Si), 835, 775, 765 (aromatic); nmr (CDCl₃, δ) 0.01 (s, 9H, Si(CH₃)₃), 4.77 (s, 1H, bridge), 6.94 (d of d, 2H, J=5 and 2Hz, ortho), 7.3-7.5 (m, 4H, meta and para); C¹³ nmr (CDCl₃, δ) 54.52 (1C, C₁, J_C-C-H = 131.8Hz), 116.7 (2C, C₂, 7), 120.88 (2C, C₄, 5), 124.98 (1C, C₃), 130.37 (2C, C₈, 6), 143.81 (2C, C₁₈, 7), 146.33 (1C, C₉), 2.50 (3C, Si(CH₃)₃); exact mass: calcd 212.1021; found 212.1020; uv max (95% EtOH) 312 nm (ε₃57), 302 (ε₅86), 282 (ε₄,530), 277 (ε₄,280), 273 (ε₄,480), 224 (ε₅8,700).


Found: C, 79.22; H, 7.59.

2) 1H-Cyclobuta[de]naphthalene (32), 15% identified by comparison with an authentic sample.

Reaction of 1H-Cyclobuta[de]naphthalenemagnesium Bromide (55) with Methyl Iodide.

1-Bromo-1H-cyclobuta[de]naphthalene (1, 1.1 g, 5 mmol) in anhydrous tetrahydrofuran (25 ml) was added to sublimed magnesium (0.12 g, 5 mmol) and the mixture was refluxed for 3.5 hr. Methyl iodide (4.54 g, 2.0 ml, 32 mmol) was added via syringe and the reaction mixture was refluxed for 48 hr, cooled to room temperature, poured into water, and extracted with ether. The ethereal extracts were washed with dilute hydrochloric acid and saturated aqueous sodium chloride, and then dried over magnesium sulfate. The
solvents were removed under reduced pressure yielding 1.0 g of a brown oily residue. Purification by molecular distillation gave 650 mg of a colorless liquid. The nmr spectrum of the product revealed it to be a mixture of 1-methyl-1H-cyclobuta[de]naphthalene (66, 80% relative yield) and 1H-cyclobuta[de]naphthalene (39, 20% relative yield). An efficient separation of the two hydrocarbons could not be affected by vapor phase or high pressure liquid chromatography. The products are identified by the nmr spectrum of the mixture: 1.67 (d, J = 7Hz, -CH₃), 4.8 (s, bridge proton of 39), 5.15 (q, J = 7Hz, bridge proton of 66), 6.88-7.0 (d of d, ortho protons), and 7.1-7.5 (m, meta and para).

Catalytic Hydrogenation of 1H-Cyclobuta[de]naphthalene (39).

1H-Cyclobuta[de]naphthalene (48 mg, 0.34 mmol) was added to a suspension of a catalytic amount of 10% Pd on carbon in dry methanol (50 ml). The mixture was hydrogenated at 20 psi for 2 hr, filtered through celite, and concentrated under reduced pressure to give 45 mg (94%) of a colorless oil. NMR analysis of the product revealed it to be 1-methylnaphthalene (62, > 95%) and a minor amount of starting hydrocarbon (< 4%). The 1-methylnaphthalene was identified by comparison with an authentic sample.
Catalytic Hydrogenation of 1-Trime thylsilyl-1H-cyclobuta[de]-naphthalene (61).

A mixture of 1-trime thylsilyl-1H-cyclobuta[de]naphthalene (160 mg, 0.75 mmol) and a catalytic amount of 10% palladium on carbon in anhydrous methanol (45 ml) was placed in a Parr hydrogenator and hydrogenated at 40 psi for 3 hr. The mixture was filtered through Celite and the methanol removed under reduced pressure to give 1-[(trime thylsilyl)methyl]naphthalene (63), 130 mg (80%), as purified by preparative vapor phase chromatography (5 ft x \( \frac{1}{4} \) in 12.5% QF-1 on chromasorb W, isothermal at 130°C); nmr (CDCl₃, 6) 0.05 (s, 9H, -Si(CH₃)₃), 2.62 (s, 2H, -CH₂), 7.1-8.1 (m, 7H, aromatic); exact mass: calcd 214.1177; found 214.1181.

Anal. Calcd for C₁₄H₁₈Si: C, 78.44; H, 8.46.

Found: C, 78.50; H, 8.57

IH-Cyclobuta[de]naphthalene-1-carboxylic Acid (64).

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (1, 440 mg, 2 mmol) and sublimed magnesium (50 mg, 2 mmol) in anhydrous ether (50 ml) was refluxed until the magnesium was completely consumed. The reaction mixture was then treated with a stream of carbon dioxide for 2 hr. The reaction was quenched by addition of 10% hydrochloric acid. The mixture was extracted with benzene, and the benzene layer washed with water. Extraction of the benzene layer with aqueous sodium hydroxide, and reprecipitation with
concentrated hydrochloric acid gave 1H-cyclobuta[de]naphthalene-1-carboxylic acid (110 mg, 30%) as a colorless solid, mp 158.5-160°; ir (KBr, cm⁻¹) 3350-2750 (OH, acid), 1750 (C = O, acid), 1475, 1410, 1290, 1210, 950, 785, 750 (aromatic); nmr (acetone-d₆, δ) 5.97 (s, 1H, bridge), 7.18 (d of d, 2H, J = 5 and 2Hz, ortho) 7.35-7.68 (m, 4H, aromatic); exact mass: calcld 184.0524; found 184.0528.

Anal. Calcld for C₁₂H₈O₂: C, 78.25; H, 4.38.  
Found: C, 77.62; H, 4.21.

Methyl 1H-Cyclobuta[de]naphthalene-1-Carboxylate (65).

Alcoholic ethereal diazomethane was prepared by charging a flask containing a solution of potassium hydroxide (7 g) in methanol (6 ml), water (5 ml), and ether (15 ml) with bis-(N-methyl-N-nitroso)-terephthalimide (70% suspension in mineral oil) at 0°. The flask was equipped with non-ground glass takeoff and attached to a receiver cooled to -78°. The mixture was gently warmed and distillation continued until the distillate was no longer yellow.

The diazomethane solution was added all at once to a solution of 1H-cyclobuta[de]naphthalene-1-carboxylic acid (40 mg, 0.217 mmol) in ether (20 ml) at -78°. The mixture was warmed to room temperature, and the excess diazomethane treated with formic acid. The mixture was extracted with saturated aqueous sodium bicarbonate, dried over magnesium sulfate and concentrated to 50 mg of a colorless oil.

Chromatography on silica gel via hexane/ether gave methyl
1H-cyclobuta[de]naphthalene-1-carboxylate (42 mg, 97.5%) as a water white liquid; ir (neat, cm⁻¹) 1735 (C=O, ester), 1260 (C-O), 1180, 1170, 1040, 790; nmr (CDCl₃, δ) 3.77 (s, 3H, -CH₃), 5.94 (s, 1H, bridge), 7.19 (d of d, 2H, J=5 and 2Hz, ortho), 7.41-7.74 (m, 4H, aromatic); exact mass: calcd 198.0680; found 198.0684.

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

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (1, 640 mg, 2.9 mmol), potassium iodide (1.5 g, 9 mmol), and a catalytic amount of 18-crown-6 in acetonitrile (30 ml) was refluxed for 60 hr. The mixture was then concentrated and taken up in pentane. Chromatography on silica gel using pentane as eluent gave 1-iodo-1H-cyclobuta[de]naphthalene (710 mg, 91%) as a colorless solid, mp 101-104⁰; ir (KBr, cm⁻¹) 1600, 1460, 1380, 1060, 1005, 980, 820, 785, 725 (aromatic); nmr (CDCl₃, δ) 6.76 (s, 1H, bridge), 7.03 (d of d, 2H, J=5 and 2Hz, ortho), 7.32-7.66 (m, 4H, meta and para); C¹³ nmr (CDCl₃, δ) 124.2 (2C, C₁₈,7ₐ), 137.8 (1C, C₈), 131.4 (2C, C₃,6 ), 126.0 (1C, C₉), 122.5 (2C, C₄,5), 115.7 (2C, C₂,7), 21.5 (1C, C₁); exact mass: calcd. 265.9594; found 265.9598; uv max (95% EtOH) 321 nm (ε706), 306 (ε1,051), 281 (ε5,500), 273 (ε6,821), 242 (ε8,312), 224 (ε59,375), 202 (ε43,125).

An analytical sample was obtained by sublimation at 75-80⁰ (0.2 mm), mp 101-104⁰.
Anal. Calcd for C_{11}H_{7}I: C, 49.65; H, 2.65.

Found: C, 49.59; H, 2.70.

1-Thiophenoxy-1H-cyclobuta[de]napthalene (68).

1-Bromo-1H-cyclobuta[de]napthalene (1, 2.19 g, 10 mmol) was added to a mixture of sodium methoxide (540 mg, 10 mmol), thiophenol (1.1 g, 1.1 ml, 10 mmol) and absolute ethanol (160 ml) and the solution was refluxed 48 hr. After the mixture had been cooled to room temperature the ethanol was removed under reduced pressure. The solid residue was dissolved in ether, and the ethereal layer washed with 1N hydrochloric acid. Drying over anhydrous magnesium sulfate and concentration under reduced pressure gave 2.9 g of a light yellow solid. The analysis of the crude product indicated the presence of two mobile fractions. The solid was absorbed onto silica gel and separated by column chromatography using n-hexane as eluent to give:

1) 1-Bromo-1H-cyclobuta[de]napthalene (1, 200 mg, 10%) identified by comparison with an authentic sample;

2) 1-Thiophenoxy-1H-cyclobuta[de]napthalene (68, 2.06 g, 83%) recrystallized from hexane at -78^°, mp 59-61^°; ir (KBr, cm^{-1}) 1590, 1460, 1170, 1080, 1030, 980, 790, 740, 630 (aromatic); nmr (CDCl$_3$, δ) 6.30 (s, 1H, bridge), 6.87-7.45 (m, 11H, aromatic);

C$^{13}$ nmr (CDCl$_3$, δ) 62.96 (1C,C$_1$), 116.5 (2C, C$_2$, 7), 122.3 (2C,
C_{45}s), 125.9 (1C, C_{3}), 127.0 (1C, C_{4} on phenyl ring), 128.7 (2C, aromatic), 130.7 (2C, aromatic), 131.1 (2C, aromatic), 135.0 (1C, C_{1} on phenyl ring), 143.7 (2C, C_{1a,7a}), 145.0 (1C, C_{8}); exact mass: calcd 248.0658; found 248.0662; analytical sample obtained by sublimation 100-105° (0.2 mm).

Anal. Calcd for C_{17}H_{11}S: C, 82.22; H, 4.87.

Found: C, 82.20; H, 4.94.

1-(Phenylsulfonyl)-1H-cyclobuta[de]naphthalene (69).

A mixture of 1-thiophenoxy-1H-cyclobuta[de]naphthalene (124 mg, 0.5 mmol) in benzene (20 ml) was stirred with m-chloroperbenzoic acid (0.5 g, 2.5 mmol) for 12 hr and then poured into water and extracted with ether. The ethereal solution was washed with 10% sodium thiosulfate and saturated sodium bicarbonate. Drying over anhydrous magnesium sulfate and removal of the solvents under reduced pressure yielded 138 mg of a white solid that was purified on a silica gel column using benzene as eluent. Recrystallization from cyclohexane gave 1-(phenylsulfonyl)-1H-cyclobuta[de]naphthalene, 125 mg (89%), mp 183-190°; ir (KBr, cm^{-1}) 1600, 1580 (aromatic), 1450 (aliphatic C-H), 1380, 1140 (SO_{2}), 1080, 845, 795, 765 (aromatic); nmr (CDCl_{3}, δ), 6.4 (s, 1H, bridge), 7.1-7.91 (m, 11H, aromatic); exact mass: calcd 280.0557; found 280.0562.

Anal. Calcd for C_{17}H_{12}O_{2}S: C, 72.83; H, 4.31.

Found: C, 72.82; H, 4.37.
1-Azido-1H-cyclobuta[de]naphthalene (70).

A mixture of sodium azide (520 mg, 8 mmol) and 1-bromo-1H-cyclobuta[de]naphthalene (440 mg, 2 mmol) in anhydrous hexamethylphosphortriamide (30 ml) was stirred at room temperature for 48-72 hr. The solution was poured into water and extracted with pentane. The pentane layer was washed several times with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give 1-azido-1H-cyclobuta[de]naphthalene as a colorless solid, 340 mg (94%), recrystallized from pentane at -78°C, mp 45-46°C; ir (KBr, cm⁻¹) 2120, 1320 (N₃, 1600, 1460, 1240, 1010, 910, 880, 780 (aromatic); nmr (CDCl₃, δ) 6.17 (bs, 1H, bridge), 7.17 (d of d, 2H, J=5 and 2Hz, ortho), 7.45-7.75 (m, 4H, meta and para); C¹³ nmr (CDCl₃, δ) 74.8 (1C, C₁), 116.9 (2C, C₂, 7), 122.9 (2C, C₄, 5), 125.8 (1C, C₆), 130.8 (2C, C₃, 6), 142.0 (2C, C₁₈, 7a), 146.0 (1C, C₈); exact mass: calcd 181.0639, found 181.0642.

Photolysis of 1-Azido-1H-cyclobuta[de]naphthalene (70) in Pentane.

A solution of 1-azido-1H-cyclobuta[de]naphthalene (700 mg, 3.9 mmol) in pentane (150 ml) was degassed with nitrogen and irradiated through quartz with a 450 W Hanovia high pressure mercury arc lamp for 140 min. Removal of the pentane under reduced pressure gave 630 mg of a black tarry mass. Two main fractions were isolated after column chromatography:
1) 1-Azido-1H-cyclobuta[de]naphthalene, 140 mg (20%); identical with an authentic sample.

2) 1-Cyanonaphthalene (71), 80 mg (13.5%); spectroscopically identical with an authentic sample. The remainder of the reaction mixture was unidentifiable material.

Thermolysis of 1-Azido-1H-cyclobuta[de]naphthalene (70) in Hexamethylphosphor triamide at 150°.

A solution of 1-azido-1H-cyclobuta[de]naphthalene (180 mg, 1 mmol) in anhydrous hexamethylphosphor triamide (3 ml) was heated at 150° for 25 min. The reaction was poured into water and extracted with ether. The ether layer was washed several times with water, dried over anhydrous magnesium sulfate, and concentrated to give 140 mg of a dark green residue. The residue was chromatographed on silica gel using 2:1 hexane/benzene as eluent. Only one product was isolated and it was determined to be 1-cyanonaphthalene (71, 120 mg, 67%); identified spectrally by comparison with an authentic sample.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Potassium Cyanide/18-Crown-6 in Methylene Chloride.33

Potassium cyanide (66 mg, 1 mmol) was added to a mixture of 1-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) and a

catalytic amount of 18-crown-6 in methylene chloride (4 ml) and the solution was refluxed for 24 hr. The cooled mixture was concentrated, dissolved in ether, and passed through a silica gel column to remove the 18-crown-6. The solvents were removed under reduced pressure yielding only starting bromide 1 (90 mg, 82%) as evidenced by nmr absorptions at δ 6.76 (s, 1H, bridge proton), 7.18 (d of d, 2H, ortho), and 7.3-7.68 (m, 4H, meta and para).

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Potassium Cyanide in Hexamethylphosphortriamide at Room Temperature.

Potassium cyanide (650 mg, 10 mmol) was added to 1-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) in anhydrous hexamethylphosphortriamide (15 ml). The mixture was stirred at room temperature for 72 hr and then poured into water and extracted with pentane. The pentane layer was washed with several portions of water, dried over magnesium sulfate and concentrated under reduced pressure to a white solid. The solid was identified as starting bromide 1 (84 mg, 76% recovery) on the basis of nmr absorptions at δ 6.76 (s, 1H, bridge proton), 7.18 (d of d, 2H, ortho), and 7.3-7.68 (m, 4H, meta and para).
Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Sodium Cyanide in Dimethylformamide at 156°.

Sodium cyanide (250 mg, 5 mmol) was added to a solution of 1-bromo-1H-cyclobuta[de]naphthalene (219 mg, 1 mmol) in dimethylformamide (20 ml). The mixture was refluxed for 5 hr, poured into water, and then extracted with ether. The ethereal solution was extracted with water and saturated sodium chloride, dried over magnesium sulfate and concentrated under reduced pressure to yield a brown intractable tar which was not investigated further.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Sodium Cyanide in Hexamethylphosphor-triamide at 90°.

A mixture of sodium cyanide (250 mg, 5 mmol) and 1-bromo-1H-cyclobuta[de]naphthalene (219 mg, 1 mmol) in hexamethylphosphor-triamide (20 ml) was heated at 90° for 24 hr, then cooled, poured into water, and extracted with ether. The organic layer was washed several times with water, dried over magnesium sulfate, and concentrated to a dark red oil which could not be further identified.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Sodium Cyanide in Hexamethylphosphor-triamide at Room Temperature.

Sodium cyanide (125 mg, 2.5 mmol) was added to a solution of 1-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) in hexamethylphosphor-triamide (10 ml). The mixture was stirred at
room temperature for 24 hr and then poured into water and extracted with ether. The ether layer was washed several times with water, dried over magnesium sulfate, and concentrated to a dark brown oil. Thin layer chromatography yielded no characterizable material.

**Reaction of 1-Bromo-lH-cyclobuta[de]naphthalene (1) with Sodium Cyanide in Absolute Ethanol at 80°.**

A mixture of sodium cyanide (250 mg, 5 mmol), 1-bromo-lH-cyclobuta[de]naphthalene (219 mg, 1 mmol) and absolute ethanol (20 ml) was refluxed for 24 hr and then cooled to room temperature. Ethanol was removed under reduced pressure to yield a solid residue which dissolved in ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated to a white solid which was identified as 1-bromo-lH-cyclobuta[de]naphthalene (185 mg, 84.5%) on the basis of nmr absorptions at δ 6.76 (s, 1H, bridge proton), 7.18 (d of d, 2H, ortho), and 7.3-7.68 (m, 4H, meta and para).

**Reaction of 1-Bromo-lH-cyclobuta[de]naphthalene (1) with Sodium Methoxide in Methanol.**

1-Bromo-lH-cyclobuta[de]naphthalene (1.1 g, 5 mmol) and sodium methoxide (1.35 g, 25 mmol) were dissolved in anhydrous methanol (50 ml) and the mixture was refluxed for 170 hr. The
solution was allowed to cool to room temperature and the methanol was removed under reduced pressure. The residue was taken up in ether and the ethereal layer was extracted with water, dried over magnesium sulfate and concentrated to a yellow oil. The oil was passed through a short silica gel column using hexane as eluent to remove the immobile yellow material. The resulting colorless liquid was separated into the following three components on a high pressure liquid chromatograph employing petroleum ether (bp 30-60°) as eluent:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (1), 88 mg (8%), identical spectrally with an authentic sample.

2) 1-Methoxy-1H-cyclobuta[de]naphthalene (78), 140 mg (16.5%) as a colorless oil; ir (neat, cm⁻¹) 2980 (aliphatic C-H), 1200, 1120 (C-O), 835, 795, 735 (aromatic); nmr (CDCl₃, 6) 3.42 (s, 3H, O-CH₃), 6.64 (s, 1H, bridge), 7.2 (d of d, 2H, J = 5 and 2Hz, ortho), 7.44-7.7 (m, 4H, meta and para); exact mass: calcd 170.0731; found 170.0733.

3) Oil, 500 mg, nmr analysis revealed this product to be a 61:39 mixture of 1-naphthaldehyde (36) and 1-naphthaldehyde dimethylacetal (79). The mixture was treated with 2,4-dinitrophenylhydrazine reagent and yielded a yellow-orange precipitate which was recrystallized from acetic acid to give 1-naphthaldehyde 2,4-dinitrophenylhydrazone in 60% overall yield; mp 250-253°, lit18 254°.
Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Sodium Methoxide in Hexamethylphosphorotriamide at 75°.

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (220 mg, 1 mmol) and sodium methoxide (60 mg, 1 mmol) in anhydrous hexamethylphosphorotriamide (5 ml) was heated at 75° for 40 hr. The reaction was poured into water and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and concentrated to a light yellow oil which was chromatographed on silica gel using 2:1 hexane/benzene as eluent. Two main fractions were isolated:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (1), 55 mg (25%), identified by comparison with an authentic sample.

2) 1-Naphthaldehyde (36), 95.5 mg (60%), identified by comparison with an authentic sample.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Aniline.

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) and aniline (46 mg, 0.5 mmol) in hexamethylphosphorotriamide (5 ml) was heated at 90° for 7 days. The mixture was poured into water and extracted with ether. The ether layer was washed with 10% aqueous hydrochloric acid, dried over anhydrous magnesium sulfate, and concentrated to an oily residue. Chromatography on silica gel using hexane/benzene as eluent yielded two main fractions:
1) 1-Bromo-1H-cyclobuta[de]naphthalene (1), 40 mg (36.5%).
2) 1-Naphthaldehyde (36), 20 mg (26%); identical spectroscopically with an authentic sample.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Piperidine.

A solution of 1-bromo-1H-cyclobuta[de]naphthalene (110 mg, 0.5 mmol) in piperidine (4 ml) was stirred at room temperature for 24 hr. The precipitate (piperidine hydrobromide) was filtered and the filtrate poured into water and extracted with ether. The ether layer was washed with 10% aqueous hydrochloric acid, dried over anhydrous magnesium sulfate, and concentrated to yield an oily residue. Chromatography on silica gel using benzene as eluent produced 1-naphthaldehyde (36, 50 mg, 64%) as the only product; identified by comparison of its infrared and nmr spectra with that of an authentic sample.

1-Triphenylphosphonium-1H-cyclobuta[de]naphthalene Bromide (83).

Triphenylphosphine (13.1 g, 50 mmol) was dissolved in xylene (150 ml). 1-Bromo-1H-cyclobuta[de]naphthalene (3.1 g, 14 mmol) was added and the mixture was refluxed for 72 hr. After cooling to room temperature the precipitate was filtered and washed with warm benzene. The solid was dried in vacuo giving 6.56 g (96.5%) of 1-triphenylphosphonium-1H-cyclobuta[de]naphthalene bromide (83). Recrystallization from ethanol-ether yielded white platelets,
mp 263-266°; ir (KBr, cm⁻¹) 3030 (aromatic C-H), 2950 (aliphatic C-H), 1600, 1450, 1010, 990, 840, 810, 770, 750, 685; nmr (DMSO-d₆, δ) 7.23 (m, 2H), 7.5-7.98 (m, 20H).


Found: C, 72.17; H, 4.72.

Reaction of 1-Triphenylphosphonium-1H-cyclobuta[de]naphthalene Bromide (83) with Sodium Dimsylate.³⁴

Sodium hydride (84 mg, 2 mmol) was added to anhydrous dimethyl sulfoxide (10 ml) and the resulting mixture was heated at 75° for 45 min. The reaction was cooled to room temperature and a solution of 1-triphenylphosphonium-1H-cyclobuta[de]naphthalene bromide (962 mg, 2 mmol) in dimethyl sulfoxide (20 ml) added via syringe. The resulting mixture was allowed to stir at room temperature for 20 min, anhydrous acetone (0.5 ml) was added, and the solution was stirred overnight. The mixture was poured into water, filtered, and extracted with pentane. The pentane layer was washed with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. NMR analysis revealed that the residue was a mixture of two hydrocarbon products. Using hexane as eluent, the residue was passed through a silica gel column to remove colored impurities. The resulting colorless solid was dissolved in pentane and cooled to -78°. The white solid which precipitated was filtered at low temperature and dried in vacuo
to give 1-isopropylidene-1H-cyclobuta[de]naphthalene (85), 172 mg (48%), mp 64.5-65.5°; ir (KBr, cm⁻¹) 1660, 1655, 1580, 1435, 1360, 1120, 820, 785; nmr (CDCl₃, δ) 2.02 (s, 6H, -CH₃), 7.04 (d of d, 2H, J = 5 and 2.5 Hz, ortho), 7.43 (m, 4H, meta and para); ¹³C nmr (CDCl₃, δ) 146.4 (1C,C₁), 145.9 (2C,C₄α,7a), 140.2 (1C,C₈), 130.4 (2C,C₃,8), 126.0 (1C), 125.3 (1C), 121.2 (2C, C₆,5), 114.1 (2C, C₂7), 20.77 (2C, -CH₃); exact mass: calcd 180.098; found 180.0942; uv max (95%) EtOH) 309 nm (ε1,856), 262 (ε17,900), 222 (ε81,700).

An analytical sample was obtained by sublimation at 63-66° (0.45 mm).

**Anal.** Calcd for C₁₄H₁₂: C, 95.29; H, 6.71.

Found: C, 92.89; H, 6.79.

The pentane mother liquor was concentrated under reduced pressure and yielded 1H-cyclobuta[de]naphthalene (79), 90 mg (32%), identified by comparison with an authentic sample.


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**Reaction of 1-Triphenylphosphonium-1H-cyclobuta[de]naphthalene Bromide (83) with n-Butyllithium in Ether at 0°.**

1-Triphenylphosphonium-1H-cyclobuta[de]naphthalene (481 mg, 1 mmol) was suspended in anhydrous ether (10 ml) under nitrogen and the mixture was cooled to 0°. n-Butyllithium (1.5 eq) was added to
the cooled solution and the mixture was allowed to warm to room
temperature. While stirring over a 2 hr period the reaction mixture
turned deep red in color. Acetone (1 ml) was added and the solution
was stirred overnight. The solvent was removed under reduced
pressure and the residue was chromatographed on a silica gel column
using hexane as eluent. A mixture of two hydrocarbons was obtained.
Separation was effected by recrystallization from pentane at -78°
giving:

1) 1H-Cyclobuta[de]naphthalene (39, 62 mg, 44%) identified
by comparison with an authentic sample.

2) 1-Isopropylidene-1H-cyclobuta[de]naphthalene (85, 65 mg,
36%), identified by comparison with an authentic sample.

1-Isopropylidene-1H-cyclobuta[de]naphthalene (85).

A suspension of 1-triphenylphosphonium-1H-cyclobuta[de]naphtha-
lene bromide (1.44 g, 3 mmol) in anhydrous tetrahydrofuran (30 ml)
was cooled to 0° and treated with t-butyllithium (4.5 mmol). The
resulting red solution was stirred at room temperature until all of
the phosphonium salt dissolved (~45 min). Anhydrous acetone (3.0
ml) was added via syringe and the resulting yellow solution was
stirred at room temperature for 1 hr. The mixture was concentrated
and separated on a silica gel column using pentane as eluent. The
yield of 1-isopropylidene-1H-cyclobuta[de]naphthalene (85) was
430 mg (80%), identical with that previously characterized.

A suspension of 1-triphenylphosphonium-lH-cyclobuta[de]-
naphthalene bromide (2.81 g, 6 mmol) in anhydrous tetrahydrofuran
(60 ml) was cooled to 0° and treated with t-butyllithium (1.5 eq). The
resulting maroon solution was stirred at room temperature until all of the phosphonium salt dissolved (~ 45 min).
Acetaldehyde (4 ml) was added, and the resulting solution was stirred at room temperature for 1 hr. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using pentane as eluent. The yield of 1-ethylidene-lH-
cyclobuta[de]naphthalene was 840 mg (84.5%). Purification by
molecular distillation gave a colorless liquid, bp 70-75° (0.22 mm);
ir (neat, cm⁻¹) 3050 (C-H), 1700 (C=C, olefinic), 1600 (C=C,
aromatic), 1480, 1440, 1370, 1310, 825, 785 (aromatic); nmr
(CDCl₃, δ) 2.0 (d, 3H, J = 6.5Hz, -CH₃), 5.8 (q, 1H, J = 6.5Hz,
olefinic), 6.93-7.27 (m, 2H, ortho), 7.34-7.59 (m, 4H, meta and
para); exact mass: calcd 166.0782; found 166.0784; uv max (95%
EtOH) 321 nm (ε932), 309 (ε1,619), 258 (ε16,621), 218 (ε74,324).

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

Found: C, 93.72; H, 6.24.

1-Benzylidene-lH-cyclobuta[de]naphthalene (87).

A mixture of 1-triphenylphosphonium-lH-cyclobuta[de]naphthalene bromide (1.45 g, 3 mmol) suspended in anhydrous tetrahydrofuran
(40 ml) was cooled to 0°. t-Butyllithium (1.5 eq) was added via syringe, and the resulting deep red solution was stirred at room temperature for 45 min. Benzaldehyde (425 mg, 4 mmol) was added, and the reaction mixture was stirred for 1.5 hr. Removal of the solvent under reduced pressure, and chromatography of the residue on silica gel using pentane as eluent, yielded 580 mg (85%) of 1-benzylidene-1H-cyclobuta[de]napthalene, recrystallized from hexane at -78°, mp 54-56; ir (KBr, cm⁻¹) 1600, 1470, 1460, 1440, 870, 815, 780, 755, 695 (aromatic); nmr (CDCl₃, δ) 6.74 (s, 1H, olefinic), 7.06-7.77 (m, 11H, aromatic); exact mass: calcd 228.0958; found 228.0945; uv max (95% EtOH) 322 nm (ε13,410), 297 (ε22,988), 287 (ε25,862), 277 (ε22,030), 222 (ε79,510).

Found: C, 94.89; H, 4.99.

1-Methylene-1H-cyclobuta[de]napthalene (88).

A suspension of 1-triphenylphosphonium-1H-cyclobuta[de]-napthalene bromide (5.62 g, 12 mmol) in anhydrous tetrahydrofuran (120 ml) was cooled to 0° and treated with t-butyllithium (17.5 mmol). The resulting maroon solution was stirred at room temperature until all of the phosphonium salt dissolved (~ 1 hr). Paraformaldehyde (2.0 g, 22.2 mmol) was added, and the resulting solution was refluxed for 2 hr. The mixture was concentrated and chromatographed on silica gel using pentane as eluent. The yield of
1-methylene-1H-cyclobuta[de]naphthalene was 1.55 g (85%). Vacuum distillation afforded a colorless liquid, bp 70° (0.45 mm); ir (neat, cm⁻¹) 3050 (C-H), 1700 (C=C, olefinic), 1630, 1590 (C=C, aromatic), 1470, 1000, 880, 825, 790, 665 (aromatic); nmr (CDCl₃, 6) 5.45 (s, 2H, olefinic), 7.16 (d of d, 2H, J = 5 and 2 Hz, ortho), 7.52 (m, 4H, meta and para); ¹³C nmr (CDCl₃, 6) 150.6 (2C, C₁₈, 7a), 149.6 (1C, C₁), 145.8 (1C, C₈), 130.6 (2C, C₃, e), 125.7 (1C, C₉), 121.9 (2C, C₄, g), 111.2 (2C, C₂, γ), 104.1 (1C, terminal olefin); exact mass: calc'd 152.0625; found 152.0628; uv max (95% EtOH) 323 nm (ϵ1,381), 311 (ϵ1,214), 257 (ϵ12,456), 221 (ϵ62,500). An analytical sample was obtained via vpc (5 ft x ¹/₄ in, 12.5% QF-1 on chromasorb W, isothermal at 115°).

**Anal.** Calcd for C₁₂H₈: C, 94.70; H, 5.30.

**Found:** C, 94.27; H, 5.54.

Catalytic Hydrogenation of 1-Isopropylidene-1H-cyclobuta[de]-naphthalene (85).

A mixture of 1-isopropylidene-1H-cyclobuta[de]naphthalene (45 mg, 0.25 mmol) and a catalytic amount of 10% palladium on carbon in anhydrous methanol (50 ml) was placed in a Parr hydrogenator; hydrogenation was effected at atmospheric pressure for 3 hr. The mixture was filtered through Celite and the methanol removed under reduced pressure to give 43 mg (95%) of a colorless
oil. Analysis via vpc revealed that the product was > 93%
1-isobutynaphthalene (82); nmr (CDCl₃, δ) 0.95 (d, 6H, -CH₃),
2.07 (m, 1H), 2.92 (d, 2H, -CH₂-), 7.17-8.1 (m, 7H, aromatic);
exact mass: calcd 184.1251; found 184.1254. An analytical sample
was obtained via vpc (5 ft x 1/4 in, 12.5% QF-1 on chromasorb W,
isothermal at 100°C).


Found: C, 91.12; H, 9.17.

1-Methyl-1H-cyclobuta[d]naphthalene (66). Diimide Reduction of
1-Methylene-1H-cyclobuta[d]naphthalene (88).

Dipotassium azodicarboxylate (9.7 g, 49 mmol) was suspended
in a solution of 1-methylene-1H-cyclobuta[d]naphthalene (490 mg,
3.2 mmol) in anhydrous methanol (75 ml). Acetic acid (7.1 g) in
methanol (50 ml) was then added dropwise over a 30 min period. The
mixture was then stirred at room temperature for 1 hr, poured into
water and extracted with pentane. The pentane layer was washed
with saturated sodium bicarbonate, dried and concentrated to a
colorless oil. Analysis of the nmr spectrum of the reaction product
revealed that only 68% reduction had taken place. The reaction
product was resubjected to the above reaction conditions and work-
up. Spectral analysis of the resulting yellow oil showed that the
olefin was > 90% reduced. An efficient separation of starting
olefin and product could not be obtained via usual techniques. The crude product mixture was subjected to m-chloroperbenzoic acid in chloroform at 0°, and worked-up as described previously.

The products were separated on a silica gel column using pentane as eluent. The yield of 1-methyl-1H-cyclobuta[de]-naphthalene was 300 mg (61%), bp 55° (0.24 mm); ir (neat, cm⁻¹) 3050 (C-H, aromatic), 2980, 2930, 2870 (C-H, aliphatic), 1600 (C=O), 1470, 1450 (C-H), 1295, 990, 810, 780 (aromatic); nmr (CDCl₃, δ) 1.67 (d, 3H, J = 7Hz, -CH₃), 5.15 (q, 1H, CHCH₃), 6.88 (d of d, 2H, aromatic), 7.1-7.5 (m, 4H, aromatic); C¹³ nmr (CDCl₃, δ) 147.4 (2C, C₁₈, C₇), 144.5 (1C, C₈), 130.4 (2C, C₄, C₅), 125.9 (1C, C₈), 121.3 (2C, C₄, C₅), 115.7 (2C, C₂, C₃), 58.2 (1C, C₁), 18.6 (1C, CH₃); exact mass: calcd 154.0782; found 154.0784; uv max (95% EtOH) 322 nm (ε91), 316 (ε261), 311 (ε382), 302 (ε478), 282 (ε4,503), 277 (ε4,358), 272 (ε4,697), 226 (ε67,796). An analytical sample was obtained by preparative vpc (5 ft x ½ in 12.5% QF-1 on chromasorb W, isothermal at 110°).

Anal. Calcd for C₁₂H₁₀: C, 93.46; H, 6.54.

Found: C, 93.28; H, 6.67.

Attempted Reduction of 1-Ethylidene-1H-cyclobuta[de]naphthalene

(86) with Diimide.

Dipotassium azodicarboxylate (750 mg, 3.8 mmol) was suspended in a solution of 1-ethylidene-1H-cyclobuta[de]naphthalene
(166 mg, 1 mmol) in anhydrous methanol (10 ml). A solution of acetic acid (470 mg, 7.8 mmol) in methanol (5 ml) was added dropwise and the mixture was stirred at room temperature for 1 hr, diluted with water, and extracted with pentane. The pentane layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give 153 mg (92%) of starting olefin (86), identified by its NMR spectrum.


1-Methyl-lH-cyclobutad[de]naphthalene (63.1 mg) was passed through a pyrex column packed with glass helices and heated to 456° at 0.1 mm of Hg. A slightly yellow liquid (50 mg, 79.5%) was collected in a trap cooled at -78°. Infrared and NMR analysis of the oil revealed it to be pure 1-vinylnapthalene (90); IR spectrum identical with Coblentz Society Spectrum #3566; NMR (CDCl3, δ)

\[ \begin{align*} 
5.28-5.92 & (m, 3H, olefinic), \\
7.17-8.17 & (m, 7H, aromatic). 
\end{align*} \]

Thermal Rearrangement of 1-Methylene-1H-cyclobuta[de]naphthalene (88).

1-Methylene-1H-cyclobuta[de]naphthalene (70 mg) was passed through a Vycor tube packed with quartz chips heated to 550° at 0.1 mm. The effluent yellow liquid (60 mg, 86%) was collected at -78° and consisted of three components on the basis of its NMR spectrum and VPC analysis. Separation and isolation via preparative VPC (10 ft x \( \frac{1}{4} \) in, 20% QF-1 on chromasorb W, isothermal at 120°)
yielded two identifiable products (91% of the mixture):

1) 1-Methylene-1H-cyclobuta[de]naphthalene (90, 6% relative yield); spectrally identical with an authentic sample.

2) 1-Ethynlnaphthalene (90, 85% relative yield); ir (neat, cm⁻¹) 3370 (C-C-H), 3100 (C-H, aromatic), 2100 (C-C), 1580, 1500, 1380, 1340, 1255, 1210, 1015, 910, 800, 770 (aromatic); nmr (CDCl₃, δ) 3.41 (s, 1H, C-C-H), 7.19-7.92 (m, 6H, aromatic) and 8.35 (m, 1H, H at C₈). The nmr and ir spectra agree with that reported in the literature.¹⁸,¹⁹

Thermal Rearrangement of 1-Ethylidene-1H-cyclobuta[de]naphthalene (86).

1-Ethylidene-1H-cyclobuta[de]naphthalene (174 mg) was passed through a Vycor tube packed with quartz chips and heated to 550° at 0.1 mm. The resulting yellow oil was collected in a trap at -78°, and determined to be a mixture of two components which were separated via preparative vpc (10 ft x 1/₄ in, 23% QF-1 on chromasorb W, isothermal at 115°).

1) 1-Ethylidene-1H-cyclobuta[de]naphthalene (86, 56% relative yield); spectrally identical with an authentic sample.

2) Methyl-1-naphthylacetylene (90, 44% relative yield); ir (neat, cm⁻¹) 3150 (C-H), 2260 (C-C), 1600, 1440, 1400, 1020, 820, 805, 780 (aromatic); nmr (CDCl₃, δ) 2.07 (s, 3H, -CH₃), 7.07-7.86 (m, 6H, aromatic), 8.45 (m, 1H, H at C₈).¹⁹
Thermal Rearrangement of 1-Benzylidene-1H-cyclobuta[de]naphthalene (87).

1-Benzylidene-1H-cyclobuta[de]naphthalene (93 mg, 0.4 mmol) was passed through a Vycor tube packed with quartz chips and heated to 650° at 0.1 mm. The effluent yellow oil (61.4 mg, 66%) was collected at -78°, and determined to be phenyl-1-naphthyl-acetylene (95); ir (neat, cm⁻¹) 3100 (C-H), 1600, 1500, 1450, 1400, 800, 795, 755 (aromatic); nmr (CDCl₃, δ) 7.19-7.9 (m, 11H, aromatic) 8.4 (m, 1H, H on C-8).

Thermal Rearrangement of 1-Isopropylidene-1H-cyclobuta[de]-naphthalene (85).

1-Isopropylidene-1H-cyclobuta[de]naphthalene (65 mg) was passed through a Vycor tube packed with quartz chips and heated to 700° at 0.1 mm. The effluent liquid was collected in a trap at -78° to produce 35 mg (54%) of a yellow oil which exhibited the following spectral properties; ir (neat, cm⁻¹) 3110, 3000, 1620, 1600, 1470, 1435, 1180, 1030, 830, 800, 775, 725 (aromatic); nmr (CDCl₃, δ) 2.2 (s), 6.0 (m), 6.45 (5), 6.65 (t), 6.95-7.7 (m, aromatic).

Irradiation of 1-Ethylidene-1H-cyclobuta[de]naphthalene (86) in Methanol.

1-Ethylidene-1H-cyclobuta[de]naphthalene (80.3 mg, 0.48 mmol) was dissolved in anhydrous methanol (10 ml) and the solution
degassed in a stream of nitrogen. The solution was irradiated through Vycor with a 450 W Hanovia high pressure mercury arc lamp for 8 hr. A brown intractable film formed on the walls of the photochemical vessel. Concentration of the yellow methanol solution under reduced pressure and chromatography on silica gel gave only starting olefin (86) (40 mg, 50\% recovery) as evidenced by its nmr spectrum.

Irradiation of 1-Ethylidene-1\textsubscript{H}-cyclobuta[de]naphthalene (86) in Pentane.

1-Ethylidene-1\textsubscript{H}-cyclobuta[de]naphthalene (145 mg, 0.87 mmol) was dissolved in purified pentane (10 ml) and the solution degassed with nitrogen. The solution was irradiated through Vycor with a 450 W Hanovia high pressure mercury arc lamp for 8 hr. The precipitated brown solid was filtered and determined to be polymeric material. Concentration of the pentane solution yielded only starting olefin (60 mg, 41\%), spectrally identical with an authentic sample.

Irradiation of 1\textsubscript{H}-Cyclobuta[de]naphthalene (32) in iso-Propanol.

1\textsubscript{H}-Cyclobuta[de]naphthalene (75 mg, 0.53 mmol) was dissolved in iso-propanol (10 ml) and the solution degassed in a stream of nitrogen. The mixture was irradiated through quartz with a 450 W Hanovia high pressure mercury arc lamp for 6 hr. Concentration of
the mixture gave a light brown residue that was chromatographed on silica gel using hexane/benzene as eluent. Only one fraction was isolated and identified as starting hydrocarbon (60 mg, 80%) by comparison of its ir and nmr spectrum with an authentic sample.

Irradiation of 1H-Cyclobuta[de]naphthalene (39) in Pentane.

1H-Cyclobuta[de]naphthalene (78.4 mg, 0.56 mmol) was dissolved in purified pentane (10 ml) and the solution degassed in a stream of nitrogen. The mixture was irradiated through quartz with a 450 W Hanovia high pressure mercury arc lamp for 3 hr. After this time an insoluble yellow precipitate had formed that was determined to be polymeric in nature as evidenced by its mass spectrum. The pentane solution was concentrated to yield only 1H-cyclobuta[de]-naphthalene (58 mg, 74%) identified on the basis of nmr absorptions at δ 4.8 (s, 2H, bridge proton), 7.1 (d of d, 2H, ortho), and 7.25-7.65 (m, 4H, meta and para).

Reaction of 1-Methylene-1H-cyclobuta[de]naphthalene (88) with Hydrogen Bromide.

A solution of 1-methylene-1H-cyclobuta[de]naphthalene (73 mg, 0.48 mmol) in methylene chloride (5 ml) was cooled in liquid nitrogen (-196°). Gaseous hydrogen bromide (0.5 mmol) was condensed into the reaction flask on a high vacuum line, and the reaction was stored at -78° for 1 hr, then at -26° overnight.
Removal of the methylene chloride under reduced pressure, and chromatography on silica gel yielded a colorless oil (110 mg) that was a mixture of three components (nmr analysis); the two major components (97% of mixture) were identified as starting olefin (83, 19%) and 1-methyl-1-bromo-1H-cyclobuta[de]naphthalene (29, 78%). Treatment of the mixture with m-chloroperbenzoic acid in chloroform at 0°, and subsequent chromatography on silica gel using pentane as eluent produced 1-methyl-1-bromo-1H-cyclobuta[de]naphthalene (86 mg, 75%) as a colorless solid. Purification was effected by sublimation, at 60-65° (0.13 mm), mp 90-92.5°; ir (KBr, cm⁻¹) 1190, 1060, 815, 780, 695 (aromatic); nmr (CDCl₃, δ) 2.47 (s, 3H, -CH₃), 7.08 (d of d, 2H, ortho) and 7.27-7.58 (m, 4H, aromatic); C¹³ nmr (CDCl₃, δ) 149.6 (2C, C₁a,7₄), 142.4 (2C, C₈), 133.1 (2C, C₃,5), 126.7 (1C, C₉), 122.7 (2C, C₄,6), 113.9 (2C, C₂,7), 70.5 (1C, C₁), 31.0 (1C, CH₃); exact mass: calcd 231.9888; found 231.9892.


3'-Methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] (101).

A mixture of 1-ethyldiene-1H-cyclobuta[de]naphthalene (166 mg, 1 mmol) dissolved in chloroform (2 ml) was slowly added to a solution of m-chloroperbenzoic acid (300 mg, 1.5 mmol) in chloroform
(10 ml) previously cooled to 0°. The mixture was placed in a refrigerator for 24 hr. The precipitated m-chlorobenzoic acid was removed by filtration. The organic layer was extracted with saturated sodium bicarbonate, 10% sodium thiosulfate, and saturated sodium chloride. Drying over anhydrous magnesium sulfate and removal of the solvent under reduced pressure gave 154 mg (85%) of 3'-methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] as a slightly yellow oil. Distillation afforded 101 as a colorless liquid, bp 81-85° (0.35 mm); ir (neat, cm⁻¹) 3030 (C-H, aromatic), 2950 (C-H, aliphatic), 1420, 1290 (C-O), 1200, 1165 (C-O), 1140, 1050, 1010, 990, 930, 850 (C-O), 830, 780, 750 (aromatic); nmr (CDCl₃, δ) 1.62 (d, 3H, J = 5Hz, -CH₃), 3.82 (q, 1H), 7.0-7.19 (m, 3H, aromatic), 7.34-7.78 (m, 4H, aromatic); exact mass: calcd 182.0731; found 182.0734.

**Anal.** Calcd for C₁₃H₁₀O: C, 85.69; H, 5.53.

**Found:** C, 85.35; H, 5.16.

**Reaction of 3'-Methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] (101) with Lithium Aluminum Hydride.**

A solution of 3'-methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] (280 mg, 1.5 mmol) in anhydrous ether (10 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (60 mg, 1.5 mmol) in ether (10 ml) over a period of 10 min. The
mixture was refluxed for 2 hr, then cooled and quenched by the addition of a saturated sodium sulfate solution. The organic layer was decanted and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a colorless oil that was chromatographed on silica gel using 3:1 hexane/ethyl acetate as eluent. The yield of α-ethyl-1-naphthalenemethanol (102) was 265 mg (95%), bp 104-110° (0.55 mm); spectrally identical with a sample prepared by independent synthesis.

α-Ethyl-1-naphthalenemethanol (102).

A solution of 1-naphthaldehyde (3.9 g, 25 mmol) in anhydrous ether (25 ml) was treated with an ethereal solution of ethylmagnesium bromide (50 mmol) at a rate that just maintained a gentle reflux. The mixture was refluxed for 2.5 hr, then cooled, and quenched by adding saturated aqueous ammonium chloride. The ether layer was decanted, and the magnesium salts were washed with ether. The combined ethereal solutions were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 4.44 g (95.5%) of α-ethyl-1-naphthalenemethanol as a colorless liquid, bp 110° (0.25 mm); ir (neat, cm⁻¹) 3380 (OH), 3050 (C-H, aromatic), 2970, 2930 (C-H, aliphatic), 1595, 1510, 1460, 1170, 1090, 1030, 970, 800, 780 (aromatic); nmr (CDCl₃, δ) 0.85 (t, 3H, -CH₃), 1.8 (m, 2H, -CH₂-), 2.58 (broad s, 1H, -OH), 5.1 (t, 1H, H-OH), 7.08-7.97 (m, 7H, aromatic); exact mass: calcd 186.1044; found 186.1046.
Boron Trifluoride Catalyzed Rearrangement of 3'-Methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] (101).

A solution of 3'-methylspiro[1H-cyclobuta[de]naphthalene-1,2'-oxirane] (394 mg, 2.16 mmol) in anhydrous methylene chloride (40 mL) was treated with freshly distilled boron trifluoride etherate (0.48 mL) at room temperature for 5 min. The reaction was quenched by adding a saturated aqueous sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and the methylene chloride removed under reduced pressure to yield 370 mg (94%) of an orange oil which consisted of 5-6 components as evidenced by tlc. The mixture was separated on a silica gel column using 6:1 hexane/ether as eluent. Two main fractions were isolated:

1) 2-Methylacenaphthenone (105), 255 mg (69%); ir (neat, cm\(^{-1}\)) 3030, 1720, 1640, 1470, 1370, 1260, 1240, 1000, 975, 910, 835, 785, 735; nmr (CDCl\(_3\), \(\delta\)) 1.49 (d, 3H, J = 7.5Hz, -CH\(_3\)), 3.55 (q, 1H, J = 7.5Hz, -CH-CH\(_3\)), 7.27-8.08 (m, 6H, aromatic); the ir and nmr spectra are identical with that reported in the literature.\(^{20}\)

2) 1H-Cyclobuta[de]naphthalen-1-yl methyl ketone (106), 45 mg (11%); ir (neat, cm\(^{-1}\)) 3100 (C-H, aromatic), 3010 (C-H, aliphatic), 1720 (C=O), 1600, 1470, 1435, 1360, 1270, 1170, 850, 800, 780 (aromatic); nmr (CDCl\(_3\), \(\delta\)) 2.3 (s, 3H, -CH\(_3\)), 5.88 (s, 1H, bridge), 7.09-7.27 (d of d, 2H, ortho), 7.34-7.76 (m, 4H, aromatic); exact mass: calcd 182.0731; found 182.0734.
An analytical sample was obtained via preparative vpc (5 ft x \( \frac{1}{4} \) in, 10\% SF-96 on chromasorb W, isothermal at 160\( ^\circ \)).

**Anal.** Calcd for C\(_{13}\)H\(_10\)O: C, 85.69; H, 5.53.

**Found:** C, 85.70; H, 5.66.

**Reaction of 1H-Cyclobuta[de]napthen-1-yl Magnesium Bromide (55)**

with Acetyl Chloride

A mixture of 1-bromo-1H-cyclobuta[de]napthalene (1, 110 mg, 0.5 mmol) and sublimed magnesium (13 mg, 0.5 mmol) in anhydrous ether was refluxed until the magnesium was completely consumed. The Grignard reagent was added by syringe to a cooled (0\( ^\circ \)) solution of acetyl chloride (1 ml) in ether (10 ml) and the reaction was stirred at 0\( ^\circ \) for 30 min, and then overnight at room temperature. The reaction was poured into water and the organic layer dried over anhydrous magnesium sulfate, and then concentrated to a light yellow oil. The oil was a mixture of at least six products (vpc analysis); one component of the mixture (21\%) exhibited a retention time identical to an authentic sample of 1H-cyclobuta[de]-napthalen-1-yl methyl ketone (106). The remainder of the material is as yet unidentified.
Reaction of 1-Isopropylidene-1H-cyclobuta[de]naphthalene (85) with Osmium Tetroxide.

A solution of 1-isopropylidene-1H-cyclobuta[de]naphthalene (90 mg, 0.5 mmol) in dioxane (15 ml) and water (5 ml) was treated with a catalytic amount of osmium tetroxide, and the reaction was stirred at room temperature for 20 min. Sodium periodate (250 mg, 1.2 mmol) was added in small portions over a period of 30 min, and the mixture stirred for an additional 2.5 hr. The reaction was poured into water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate, and the solvents removed under reduced pressure to yield a black amorphous residue that was not characterized further.

1H-Cyclobuta[de]naphthalen-1-one (108).

A solution of 1-isopropylidene-1H-cyclobuta[de]naphthalene (85, 900 mg, 5 mmol) in anhydrous ethyl acetate (75 ml) was cooled to -78°C and ozonized. The cold ozonide solution was treated with dimethyl sulfide (5 ml) and the resulting mixture stirred at room temperature for 5 hr. Removal of the solvent under reduced pressure gave a dark brown oil which was chromatographed on silica gel using 2:1 hexane/benzene as eluent. Two fractions were isolated:

1) 1-Isopropylidene-1H-cyclobuta[de]naphthalene (85), 125 mg (29%), identical with an authentic sample.
2) 1H-Cyclobuta[de]naphthalen-1-one (108), 250-mg (71%), sublimed at 40-41°C (0.15 mm), mp 51.5-53.5°C; ir (KBr, cm⁻¹) 1820 (m), 1775 (vs, C=O), 1660, 1410, 1300, 1225, 820, 795 (aromatic); nmr (CDCl₃, δ) 7.34 (d of d, 2H, J = 6 and 2 Hz), 7.5-7.90 (m, 4H); c¹³ nmr (CDCl₃, δ) 178.2 (1C, C₁), 162.1 (1C, C₈), 156.0 (2C, C₁₈, γ₈); 131.4 (2C, C₃, C₆), 127.3 (1C, C₉), 124.9 (2C, C₄, s), 116.8 (2C, C₁, γ₁); exact mass: calcd 154.0418; found 154.0421; uv max (95% EtOH, nm) 342 (ε2, 105), 330 (ε1, 606), 297 (ε2, 548), 280 (ε1, 487), 267 (ε5, 041), 223 (ε85, 318).

Found: C, 85.62; H, 3.94.

1-Chloro-1-thiophenoxycyclobuta[de]naphthalene (110).

A mixture of N-chlorosuccinimide (800 mg, 6 mmol) and 1-thiophenoxycyclobuta[de]naphthalene (68, 1.24 g, 5 mmol) in carbon tetrachloride (25 ml) was refluxed overnight. Removal of the solvent under reduced pressure, and recrystallization of the residue from hexane at -78°C gave 1.56 g (92.5%) of 1-chloro-1-thiophenoxycyclobuta[de]naphthalene (110, mp 74-75°C); nmr (CDCl₃, δ) 6.93 (d of d, 2H, aromatic), 7.14-7.67 (m, 9H, aromatic); c¹³ nmr (CDCl₃, δ) 83.8 (1C, C₁), 115.8 (2C, C₂, γ), 122.6 (2C, C₄, s), 126.3 (1C, C₈), 128.3 (2C, aromatic), 128.7 (2C, aromatic), 130.4 (2C, aromatic), 133.0 (1C, C₁ on phenyl ring), 134.9 (2C, aromatic), 142.7 (1C, C₈), 147.2 (2C, C₁₈, γ₈); mass spectrum m/e 282 (M⁺).

The hydrolysis of 1-chloro-l-thiophenoxy-lH-cyclobuta[de]-naphthalene was carried out under a variety of conditions. Typically, 1-3 mmol of chlorosulfide and two equivalents of the hydrolytic reagent were stirred at 20-25° for 24-48 hr. The organic layer was dried over magnesium sulfate, and the products separated via preparative thin-layer chromatography using 2:1 hexane/benzene as eluent.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Isolated Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Aqueous sodium carbonate (24 hr)</td>
<td>Ketone (108, &lt;5%); Chlorosulfide (110, 38%).</td>
</tr>
<tr>
<td>2. Aqueous HgCl₂/CdCO₃</td>
<td>Ketone (&lt;5%); Chlorosulfide (53%); Diphenyldisulfide.</td>
</tr>
<tr>
<td>3. Chloroamine-T, aqueous methanol</td>
<td>Methyl napthoate (14%).</td>
</tr>
<tr>
<td>4. Aqueous sodium carbonate (48 hr)</td>
<td>Ketone (12%); Chlorosulfide (41%).</td>
</tr>
</tbody>
</table>

Attempted Photodecarbonylation of Acenaphthenequinone (109)

Acenaphthenequinone (109, 3.64 g, 20 mmol) was suspended in purified hexane (170 ml, degassed with nitrogen) and irradiated through a Vycor filter for 67 hr with a 450 W high pressure mercury arc lamp. Tlc analysis did not reveal the presence of a reaction product, only starting quinone 109 (3.2 g, 88% recovery).
Reaction of 1H-Cyclobuta[de]naphthalen-1-one (108) with Methanol.

A solution of 1H-cyclobuta[de]naphthalen-1-one (90 mg, 0.584 mmol) in anhydrous methanol (5 ml) was stirred overnight at room temperature. Removal of the methanol under reduced pressure and chromatography on silica gel using hexane/benzene as eluent gave a colorless oil which eventually solidified. The yield of 1-methylnaphthoate was 75 mg (69%), mp 58-60\(^\circ\), lit\(^{35}\) 60\(^\circ\); ir (neat, cm\(^{-1}\)) 3100 (C-H, aromatic), 3020 (C-H, aliphatic), 1730 (C=O, ester), 1600, 1580, 1520, 1455, 1220, 1240, 1190, 1130, 1070, 1030, 1020, 845, 815, 780; nmr (CDCl\(_3\), \(\delta\)) 3.97 (s, 3H, -CH\(_3\)), 7.32-8.26 (m, 6H, aromatic), 8.81-9.02 (m, 1H, H at C\(_8\)); exact mass: calcd 186.0680; found 186.0683.


Reaction of 1H-Cyclobuta[de]naphthalen-1-one (108) with Potassium Hydroxide in Hexamethylphosphortriamide.

A solution of 1H-cyclobuta[de]naphthalen-1-one (30 mg, 0.19 mmol) in anhydrous hexamethylphosphortriamide (~ 2 ml) was treated with a small amount of potassium hydroxide and the resulting mixture stirred at room temperature for 3.5 hr. After this period of time no trace of ketone remained as evidenced by tlc. The reaction was
poured into water, treated with 1\textsuperscript{N} hydrochloric acid, and the precipitated white solid filtered and dissolved in benzene. The benzene solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1-naphthoic acid (30 mg, 88\%) as a white solid, mp 160-162\(^\circ\) C, lit\textsuperscript{3s} 160-161\(^\circ\) C; ir spectrum identical with Sadtler Standard Spectrum \#2162.

Reaction of 1\textsubscript{H}-Cyclobuta[de]naphthalen-l-one (108) with Aniline.

A solution of 1\textsubscript{H}-cyclobuta[de]naphthalen-l-one (77 mg, 0.5 mmol) in benzene (10 ml) was treated with distilled aniline (46 mg, 0.5 mmol) and heated on a steam bath for 4 hr. Removal of the solvent under reduced pressure produced a slightly yellow solid. The yield of 1-naphthanilide (115) was 100 mg (80.5\%), mp 160-163, lit\textsuperscript{3s} 163\(^\circ\) C; ir (KBr, cm\textsuperscript{-1}) 3400 (N-H), 1660 (C=O), 1600, 1535, 1440, 1320, 1250, 785, 770, 750 (aromatic); exact mass: calcd 247.0997; found 247.1000.


Reaction of 1\textsubscript{H}-Cyclobuta[de]naphthalen-l-one (108) with 2,4-
Dinitrophenylhydrazone in Sulfuric Acid.

1\textsubscript{H}-Cyclobuta[de]naphthalen-l-one (77 mg, 0.5 mmol) was added to a solution of 2,4-dinitrophenylhydrazone (99 mg, 0.5 mmol) in
concentrated sulfuric acid (2 ml). An immediate and violent reaction ensued, and the reaction was poured onto crushed ice. The resulting tan solid was filtered and dried under reduced pressure to yield 50 mg (58%) of 1-naphthoic acid, mp 159-161°; identical spectrscopically with an authentic sample.

Reaction of 1H-Cyclobuta[de]naphthalen-1-one (108) with Triphenylphosphonium methyldide.

Methyltriphenylphosphonium bromide (179 mg, 0.5 mmol) in anhydrous tetrahydrofuran (10 ml) was cooled to 0°, and then treated with t-butyllithium (1.5 eq). The mixture was warmed to room temperature and stirred until a homogeneous solution resulted. The solution was cooled to -78° and 1H-cyclobuta[de]naphthalen-1-one (77 mg, 0.5 mmol) in tetrahydrofuran (10 ml) was added by syringe. The reaction was stirred at -78° for 1 hr, and then slowly warmed to room temperature. TLC indicated that no hydrocarbon product was present. Aqueous sodium hydroxide was added and the mixture refluxed for 24 hr. The reaction was poured into water and extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to a dark oily residue that was chromatographed on silica gel using benzene as eluent. Only one fraction was isolated and it was identified as 1-acetonaphthalene (118, 25 mg, 17.5%) by comparison of its infrared and nmr spectra with that of an authentic sample.
Thermolysis of $\text{1H-Cyclobuta[de]naphthalen-1-one (108)}$ in Dimethyl Acetylenedicarboxylate at 350°.

A solution of $\text{1H-cyclobuta[de]naphthalen-1-one (77 mg, 0.5 mmol)}$ in dimethyl acetylenedicarboxylate (3 ml) was slowly dropped onto a Vycor tube that was packed with quartz chips and heated to 350° at 0.1 mm. Column chromatography on silica gel using 3:1 chloroform/benzene as eluent yielded no identifiable material. Mass spectrometry did not reveal the presence of the expected adducts or any molecular fragments derived therefrom.

Thermolysis of $\text{1H-Cyclobuta[de]naphthalen-1-one (108)}$ in Dimethyl Acetylenedicarboxylate.

A mixture of $\text{1H-cyclobuta[de]naphthalen-1-one (77 mg, 0.5 mmol)}$ in dimethyl acetylenedicarboxylate (1 ml) was heated at 180° for 30 min. Removal of the dimethylacetylenedicarboxylate under reduced pressure and chromatography on silica gel using 3:1 chloroform/benzene as eluent produced starting ketone (108, 15%) along with intractables.

Thermolysis of $\text{1H-Cyclobuta[de]naphthalen-1-one (108)}$ in Cumene.

A solution of $\text{1H-cyclobuta[de]naphthalen-1-one (60.3 mg, 0.39 mmol)}$ in cumene (4 ml) was refluxed for 2 hr. Removal of the cumene under reduced pressure produced an oily residue which did
not contain any volatile components via vpc. Chromatography of
the residue on silica gel using benzene as eluent gave only
starting ketone (20 mg, 33%) along with intractables.

Irradiation of 1H-Cyclobuta[de]naphthalen-1-one (108) in Dimethyl
Acetylenedicarboxylate.

A solution of 1H-cyclobuta[de]naphthalen-1-one (68.8 mg,
0.45 mmol) and dimethyl acetylenedicarboxylate (1 ml) in 6:1
pentane/benzene was degassed in a stream of nitrogen. The mixture
was irradiated with a 450 W Hanovia high pressure mercury arc
lamp for 1000 min. Removal of the solvents in vacuo produced a
brownish oil that was chromatographed on silica gel using 4:1
chloroform/benzene as eluent. The resulting yellow oil could not
be identified.

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) and 9-Bromo-
Fluorene with Ethanolic Silver Nitrate.

9-Bromofluorene was dissolved in ethanol (95%) and a 2%
ethanolic silver nitrate solution was added rapidly. An immediate
precipitate of silver bromide ensued.

1-Bromo-1H-cyclobuta[de]naphthalene in ethanol (95%) was
treated with a 2% ethanolic silver nitrate solution. The mixture
became only slightly cloudy after 4 min at room temperature. After
warming the solution on a water bath for 2 min, a definite precipitate of silver bromide was observed.

1-Acetoxy-1H-cyclobuta[de]naphthalene (124).

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (l, 1.1 g, 5 mmol), silver acetate (900 mg, 5 mmol), and anhydrous sodium acetate (1.0 g, 12.5 mmol) in dry hexamethylphosphorotriamide (40 ml) was heated at 75° for 24 hr. The dark brown mixture was poured into water and extracted with ether. The organic layer was washed several times with water, dried over magnesium sulfate and concentrated to 380 mg of a slightly yellow oil. The mixture was separated on a silica gel column using a 2:1 hexane/benzene mixture as eluent. Two main fractions were isolated:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (l), 80 mg (7.3%); identified by comparison with an authentic sample.

2) 1-Acetoxy-1H-cyclobuta[de]naphthalene (124), 850 mg (86%), bp 85-90° (0.15 mm); ir (neat, cm⁻¹) 3040 (C-H, aromatic), 2940 (C-H, aliphatic), 1740 (C=O, ester), 1470, 1375, 1230 (C-O), 1070 (C-O), 960, 930, 820, 790 (aromatic); nmr (CDCl₃, δ) 2.05 (s, 3H, OCC₃), 7.0-7.28 (m, 3H, ortho and bridge), 7.34-7.67 (m, 4H, meta and para); c¹³ nmr (CDCl₃, δ) 170.6 (1C, C=O), 146.8 (1C,C₈), 143.0 (2C,C₈), 130.9 (2C,C₈), 126.1 (1C,C₈), 122.8 (2C,C₈), 117.0 (2C,C₂,γ), 84.7 (1C,C₁), 20.8 (1C,-CH₃); exact mass: calcd 198.0680; found 198.0684; uv max (95% EtOH) 317 nm (ε931),
312 (e987), 303 (e1,056), 282 (e4,375), 277 (e4,187), 272 (e4,312), 221 (e66,200). An analytical sample was obtained as its picrate.

1-Acetoxy-1H-cyclobuta[de]naphthalene Picate

1-Acetoxy-1H-cyclobuta[de]naphthalene (12b, 100 mg, 0.5 mmol) in benzene (2 ml) was added to a solution of picric acid (115 mg, 0.5 mmol) in benzene (3 ml). The resulting greenish-yellow solution was allowed to evaporate overnight. The yellow solid which precipitated in quantitative yield was recrystallized from ether at \(-78^\circ\), mp 113-115\(^\circ\).

Anal. Calcd for C\(_{16}\)H\(_{16}\)O\(_{9}\): C, 53.40; H, 3.06.

Found: C, 53.34; H, 3.10.

Reaction of 1-Acetoxy-1H-cyclobuta[de]naphthalene (12b) with Potassium Carbonate in Ethanol.

1-Acetoxy-1H-cyclobuta[de]naphthalene (147 mg, 0.74 mmol) was added to a solution of potassium carbonate (690 mg, 5 mmol) in ethanol (12 ml) and the mixture was stirred at 20-25\(^\circ\) for 6 hr. The reaction was poured into water and extracted with ether. The ethereal extracts were washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave a colorless oil which was identified as 1-naphthaldehyde (36, 80 mg, 70\%) by comparison of its nmr and ir spectra to that of an authentic sample.
Reaction of 1-Acetoxy-1H-cyclobuta[de]naphthalene (12k) with Lithium Aluminum Hydride.

1-Acetoxy-1H-cyclobuta[de]naphthalene (100 mg, 0.5 mmol) in anhydrous ether (5 ml) was treated with a slurry of lithium aluminum hydride (10 mg, 0.25 mmol) in ether (2 ml) for 10 min. The reaction was then hydrolyzed by adding a saturated aqueous sodium sulfate solution. The ether layer was decanted and the aluminum salts washed with ether. The combined ether solutions were dried over anhydrous sodium sulfate and the solvents removed under reduced pressure to yield a yellow oil which consisted of two components as evidenced via tlc. Separation on a silica gel column using 2:1 hexane/benzene and 1:1 hexane/ethyl acetate as eluents produced two main fractions:

1) 1-Acetoxy-1H-cyclobuta[de]naphthalene (12k), 35 mg (35%), identified by comparison with an authentic sample.

2) 1-Naphthalenemethanol (126), 50 mg (63%), ir spectrum identical with Sadtler Standard Spectrum #17258; nmr (CDCl₃, δ) 2.33 (broad s, 1H, exchangeable, OH), 5.0 (s, 2H, -CH₂-), 7.2-8.1 (m, 7H, aromatic).
Reaction of 1-Acetoxy-1H-cyclobuta[de]naphthalene (124) with Methanolic Hydrochloric Acid.

1-Acetoxy-1H-cyclobuta[de]naphthalene (128 mg, 0.65 mmol) in anhydrous methanol (10 ml) was treated with concentrated hydrochloric acid (4 drops) and the mixture was refluxed for 5.5 hr. The reaction was concentrated under reduced pressure and then poured into water, and extracted with ether. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated to a colorless oil (90 mg). Analysis of the nmr spectrum of the reaction product revealed it to be a mixture of 1-naphthaldehyde (36, 68% relative yield), and 1-naphthaldehyde dimethyl acetal (79, 32% relative yield). The reaction products were isolated in 82% overall yield and identified by the nmr spectrum of the mixture which exhibited absorptions at 6 3.3 (s, 6H, -OCH₃ of dimethyl acetal), 5.84 (s, 1H, CH(OCH₃)₂), 7.34-8.0 (m, 12H, aromatic), 8.3 (m, 1H, peri proton of acetal), 9.15 (m, 1H, peri proton of 1-naphthaldehyde), and 10.02 (s, 1H, CHO).

Reaction of 1-Bromo-1H-cyclobuta[de]naphthalene (1) with Silver Acetate in Acetic Acid.

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (440 mg, 2 mmol) and silver acetate (340 mg, 2 mmol) in glacial acetic acid (20 ml) was heated at 75°C for 38.5 hr, cooled, poured into
water, and extracted with ether. The ethereal solution was washed with water and saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated to yield 450 mg of a solid material. The material was separated by column chromatography on silica gel using 4:1 hexane:ethyl acetate as eluent. Three main fractions were isolated:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (1), 70 mg (16%), identical spectrally with an authentic sample.

2) 1-Naphthaldehyde (36), 90 mg (29%), identical with an authentic sample.

3) α,α-Diacetoxy-1-methylnaphthalene (127), 270 mg (55%), mp 106-108.5° purified by sublimation at 100° (0.2 mm); ir (KBr, cm⁻¹) 1760, 1740 (C=O), 1400, 1240, 1210 (C-O); nmr (CDCl₃, δ) 2.09 (s, 6H, OCOCH₃), 7.32-7.88 (m, 6H, aromatic), 8.1-8.25 (m, 2H, 1 aromatic and H-C(OAc)₂); exact mass: calcd 258.0891; found 258.0896.


Found: C, 70.00; H, 5.44.

Reaction of 1H-Cyclobuta[de]naphthalene (39) with Silver Acetate in Acetic Acid at 75°:

A mixture of 1H-cyclobuta[de]naphthalene (70 mg, 0.5 mmol) and silver acetate (83 mg, 0.5 mmol) in glacial acetic acid (3 ml)
was heated at $75^\circ$ for 16 hr. The reaction was poured into water and extracted with ether. The ether extracts were washed with saturated aqueous sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 1-naphthenemethanol acetate (129, 84.5 mg, 84.5%) as a colorless oil; ir (neat, cm$^{-1}$) 3100 (C-H, aromatic), 3000 (C-H, aliphatic), 1750 (C=O, ester), 1520, 1470, 1440, 1370, 1230 (C-O), 1060, 1030, 965, 800, 775 (aromatic); nmr (CDCl$_3$, $\delta$) 2.03 (s, 3H, -CH$_3$), 5.53 (s, 2H, -CH$_2$-), 7.34-8.09 (m, 7H, aromatic).

1-H-Cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (130).

A mixture of 1-bromo-1H-cyclobuta[de]naphthalene (I, 1.1 g, 5 mmol) and silver tosylate (1.4 g, 5 mmol) in anhydrous hexamethylphosphortriamide (25 ml) was heated at $75^\circ$ for 50 hr. The reaction was poured into water and extracted with ether. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to a yellow oil which solidified upon standing. The mixture was separated on silica gel using hexane/benzene as eluents. Three main fractions were isolated:

1) 1-Bromo-1H-cyclobuta[de]naphthalene (I), 280 mg (25%), spectroscopically identical with an authentic sample.
2) l-Naphthaldehyde (36), 100 mg (12.7%), identified spectrally by comparison with an authentic sample.

3) lH-Cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (130), 680 mg (45%), recrystallized from Petroleum Ether (bp 30-60°) at -78°; ir (KBr, cm⁻¹) 1600, 1420, 1365, 1330, 1180 (SO₂), 1175 (SO₂), 1090, 1055, 995, 940, 860, 805, 785 (aromatic); nmr (CDCl₃, δ) 2.43 (s, 3H, -CH₃), 6.83-8.03 (m, 11H, aromatic and bridge); C¹³ nmr (CDCl₃, δ) 146.6 (1C, quaternary), 145.2 (1C, quaternary), 141.4 (2C, C₁₈₋₇₈), 133.5 (1C, C₄'), 131.0 (2C, aromatic), 129.9 (2C, aromatic), 128.3 (2C, aromatic), 126.1 (1C, C₇), 123.2 (2C, C₄₅), 117.0 (2C, C₈₋₇), 87.4 (1C, C₁), 21.6 (1C, -CH₃); exact mass: calc'd 310.0663; found 310.0668.

Anal. Calcd for C₁₈H₁₄O₅S: C, 69.66; H, 4.54

Found: C, 69.27; H, 4.67.

Solvolysis of lH-Cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (130) in Acetic Acid at 75°.

A solution of lH-cyclobuta[de]naphthalen-1-yl p-toluene-sulfonate (100 mg, 0.32 mmol) in glacial acetic acid (3 ml) was heated at 75° for 27 days. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with water, saturated aqueous sodium bicarbonate, and dried over magnesium sulfate. Removal of the solvent under reduced pressure produced a
light brown oily residue that was chromatographed on silica gel using 6:1 hexane/ether as eluent. Two main fractions were collected:

1) 1H-Cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (150, 12.5 mg, 12.5%).

2) 1-Naphthaldehyde (36), 0.41 mg (82%); spectrally identical with an authentic sample.

Reaction of 1H-Cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (130) with Acetic Acid at 75° for 5 days.

A solution of 1-H-cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (102.6 mg, 0.33 mmol) in glacial acetic acid (3 ml) was heated at 75° for 5 days. The reaction mixture was poured into water and extracted with ether. The ether extracts were washed with water, saturated aqueous sodium bicarbonate, dried over magnesium sulfate and concentrated to a slightly yellow oil (80 mg). NMR analysis revealed that the product was a 82:15:3 mixture of 1H-cyclobuta[de]naphthalen-1-yl p-toluenesulfonate (130), 1-acetoxycyclobuta[de]naphthalene (124), and 1-naphthaldehyde (36) by comparison with the nmr spectra of authentic samples.
Attempted Acetic Acid Catalyzed Rearrangement of 1-Acetoxy-1H-cyclobuta[de]naphthalene (12h).

1-Acetoxy-1H-cyclobuta[de]naphthalene (50 mg, 0.25 mmol) dissolved in glacial acetic acid (~2 ml) was heated at 75° for 43 hr. The reaction was poured into water and extracted with ether. The ether layer was washed with saturated aqueous sodium bicarbonate, water, and then dried over magnesium sulfate. Removal of the solvent in vacuo gave 44 mg of a colorless oil which was identified as starting acetate (88% recovery) on the basis of its spectral properties.

Reaction of 1-Acetoxy-1H-cyclobuta[de]naphthalene (12h) with Acetic Acid at 75°.

1-Acetoxy-1H-cyclobuta[de]naphthalene (110 mg, 0.55 mmol) in glacial acetic acid (3 ml) was heated at 75° for 25 days. The reaction was poured into water and extracted with ether. The ether layer was washed with water, saturated aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo produced a colorless oil (100 mg) which was shown to be a 4:1 mixture of 1-acetoxy-1H-cyclobuta[de]-naphthalene (12h) and 1-naphthaldehyde (36) by nmr analysis.
Reaction of 1H-Cyclobuta[de]naphthalene (32) with N-Bromosuccinimide.

1H-Cyclobuta[de]naphthalene (140 mg, 1 mmol) was added to a suspension of N-bromosuccinimide (720 mg, 4 mmol) in distilled carbon tetrachloride (15 ml) containing a small amount of benzoyl peroxide as a free radical initiator. The mixture was refluxed for 4.5 hr under nitrogen. The reaction was cooled to room temperature and filtered to remove the succinimide. The filtrate was extracted with saturated aqueous potassium carbonate, and distilled water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 147 mg of a yellow oil which was purified on a silica gel column using hexane as eluent. NMR analysis of the oily product revealed it to be a mixture of 1-bromo-1H-cyclobuta[de]naphthalene (1, 40% overall yield), and 1H-cyclobuta[de]naphthalene (32, 56% overall recovery).

Irradiation of 1-Bromo-1H-cyclobuta[de]naphthalene (1) in Cumene.

A solution of 1-bromo-1H-cyclobuta[de]naphthalene (55 mg, 0.25 mmol) in distilled cumene (5 ml) was degassed in a stream of nitrogen. The mixture was irradiated through quartz with a 450 W Hanovia high pressure mercury arc lamp for 45 min. Gas chromatographic analysis (5 ft x \( \frac{1}{4} \) in, 10% SF-96 on chromasorb W, isothermal at 135°C) revealed that starting bromide 1 was completely consumed and that 1H-cyclobuta[de]naphthalene (39, 60% relative to an
internal standard) was the only volatile product. Hydrocarbon \textsuperscript{39} was identified by comparison of its vpc retention time with that of an authentic sample.

Irradiation of 1-Bromo-1H-cyclobuta[de]naphthalene (1) in Ethyl Ether.

1-Bromo-1H-cyclobuta[de]naphthalene (219 mg, 1.0 mmol) in anhydrous ethyl ether (10 ml) was irradiated through pyrex for 4.5 hr with a 450 W Hanovia high pressure mercury arc lamp. The mixture was concentrated and purified by column chromatography on silica gel using n-hexane as eluent. The only products isolated were starting bromide 1 \textsuperscript{2} 179 mg (81.5\%) and 1H-cyclobuta[de]-naphthalene (\textsuperscript{39}), 5\% based on vpc analysis.

Acenaphthene-5,6-dicarboxylic Acid Di-N,N-dimethylamide.

Acenaphthene-5,6-dicarboxylic acid di-N,N-dimethylamide was prepared according to the method of Trost \textsuperscript{28} in 66\% yield from acenaphthene. Recrystallization from ethanol-water gave colorless crystals, mp 112-114\,\degree, lit 112-114\,\degree; ir (KBr, cm\textsuperscript{-1}) 1630 (C=O, amide); nmr (CDCl\textsubscript{3}, \delta) 2.87 (s, 6H, N-CH\textsubscript{3}), 3.09 (s, 6H, N-CH\textsubscript{3}), 3.40 (s, 4H, benzylic protons), 7.30 and 7.37 (AB quartet, 4H, J = 7Hz); exact mass: calcd 296.1524; found 296.1528.
Acenaphthene-5,6-dicarboxylic Acid (136).

Acenaphthene-5,6-dicarboxylic acid was prepared according to the method of Trost in 77.5% yield from acenaphthene-5,6-dicarboxylic acid di-N,N-dimethylamide; nmr (dmso-\(d_6\), 6) 3.36 (s, 4H, bridge), 7.36 and 7.91 (AB quartet, 4H, \(J=7\)Hz, aromatic).

Anhydro-6-hydroxymercuri-5-acenaphthenoic Acid (137).

Acenaphthene-5,6-dicarboxylic acid (22.4 g, 0.1 mol) and sodium hydroxide (14 g, 0.35 mol) in water (600 ml) was heated at reflux until all solids dissolved. Mercuric acetate (35 g, 0.11 mol) dissolved in water (100 ml) and glacial acetic acid (20 ml) was added to the sodium 5,6-acenaphthenalate solution. After the solution was refluxed for ~30 min, additional acetic acid (30 ml) was added to adjust the pH to 5. The mixture was refluxed 48 hr, cooled to room temperature and filtered. The resulting tan solid was washed with distilled water, and dried in vacuo at 80° overnight. The yield of anhydro-6-hydroxymercuri-5-acenaphthenoic acid was 39.4 g (99%).

6-Bromo-5-acenaphthenecarboxylic Acid (138).

A mixture of anhydro-6-hydroxymercuri-5-acenaphthenoic acid (19.8 g, 50 mmol) in glacial acetic acid (76 ml) and water (12 ml) vigorously stirred and cooled to 0° in an ice bath. A solution of
sodium bromide (3.4 g, 0.33 mol) in water (62 ml) and bromine (8.1 g, 2.8 ml, 50 mmol) was added slowly while maintaining a reaction temperature of 0-5°. The resulting slurry was then heated to 100° and poured into ice-water (300 ml). The resulting tan solid was filtered, washed with water and dried in vacuo. Recrystallization from ethanol gave 11.15 g (81%) of 6-bromo-5-acenaphthenecarboxylic acid, mp 270-277°, lit29 285-290; ir (KBr, cm⁻¹) 2700-3300 (acid OH), 2650 (C-H), 1690 (C=O, acid), 1600, 1500, 1400, 1280, 1260, 1220, 1110, 1030, 880, 850, 770 (aromatic); nmr (dmsod6, δ) 3.32 (s, 4H, benzylic), 7.19-7.86 (m, 4H, aromatic); exact mass: calcd 275.9786; found 275.9792.

Methyl 6-bromo-5-acenaphthenecarboxylate (139).

A solution of 6-bromo-5-acenaphthenecarboxylic acid (10.94 g, 40 mmol) in ether (200 ml) and methanol (200 ml) was cooled to -20° and treated with ethereal diazomethane (2 eq) previously cooled to -78°. The mixture was allowed to warm to room temperature and stirred for 1 hr. Formic acid was added until nitrogen evolution ceased, and then the mixture was extracted with aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting solid was recrystallized from ethanol to give methyl-6-bromo-5-acenaphthenecarboxylate (10.6 g, 91%) as a colorless solid, mp 109.5-111.5°; ir (KBr, cm⁻¹) 1735
(C=O, ester), 1600, 1500, 1435, 1280, 1220, 1110, 1075, 1040, 970, 890, 809, 790, 780, 690; nmr (CDCl₃, δ) 3.17 (s, 3H, -CH₃), 3.93 (s, 4H, benzylic), 6.91-7.66 (2 AB quartets, 4H, J = 7.0 and 7.5Hz, aromatic); mass spectrum 290, 292 (M⁺).

Found: C, 57.58; H, 3.89.

**Attempted Reduction of Methyl 6-bromo-5-acenaphthenecarboxylate (139) with Diisobutylaluminum Hydride**

Diisobutylaluminum hydride (4 ml, 4 mmol, 25% solution in hexane) was slowly added to a solution of methyl 6-bromo-5-acenaphthenecarboxylate (582 mg, 2 mmol) in anhydrous ether (30 ml) which was cooled to 0°. The reaction was refluxed for 48 hr, cooled to room temperature, and hydrolyzed by the addition of 10% aqueous hydrochloric acid. The ether layer was extracted with saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and the solvent removed under reduced pressure to give 570 mg (98%) of starting ester as evidenced by nmr absorptions at δ 3.17 (s, 3H), 3.93 (s, 4H), and 6.91-7.66 (2 AB quartets, 4H).

**Reaction of Methyl 6-bromo-5-acenaphthenecarboxylate (139) with Red-al.**

A mixture of methyl 6-bromo-5-acenaphthenecarboxylate (582 mg, 2 mmol), anhydrous ether (30 ml) and bis(2-methoxyethoxy)-aluminum hydride (600 mg, 2 mmol, 70% solution in benzene) was
refluxed for 5 hr and then quenched by adding a saturated aqueous sodium sulfate solution. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield 330 mg of a colorless solid which was identified as 5-acenaphthencarboxaldehyde (90%), mp 155-157° (benzene), lit37 155-157°.


6-Bromo-5-acenaphthenemethanol (140).

Lithium aluminum hydride (140 mg, 3.4 mmol) was added in small portions to a solution of methyl 6-bromo-5-acenaphthene-carboxylate (2.0 g, 6.8 mmol) in anhydrous ether (100 ml). The reaction was stirred at room temperature until all of the ester was reduced (tlc analysis). The reaction was hydrolyzed by addition of saturated aqueous sodium sulfate. The ether layer was dried over magnesium sulfate and the solvent removed under reduced pressure to afford 1.64 g (90.5%) of a slightly yellow solid which consisted of a 95:5 mixture of 6-bromo-5-acenaphthenemethanol (140) and 5-acenaphthenemethanol (141) respectively (nmr analysis). Recrystallization from cyclohexane afforded 6-bromo-5-acenaphthenemethanol (98% pure, mass spectral analysis) as a colorless solid, mp 108-110; ir (KBr, cm⁻¹) 3400 (OH), 3000 (CH), 1600, 1435, 1080,
(C-O), 1040, 1015, 840, 815 (aromatic); nmr (CDCl$_3$, δ) 3.28 (s, 4H, benzylic), 5.30 (s, 2H, -CH$_2$-), 6.97-7.76 (m, 4H, aromatic), 2.33 (broad s, 1H, OH); exact mass: calc'd 261.9993; found 261.9998.

6-Bromo-5-acenaphthenecarboxaldehyde (142).

N-chlorosuccinimide (4.0 g, 30 mmol) in toluene (125 ml) was cooled to 0°. Dimethyl sulfide (1.86 g, 2.3 ml, 30 mmol) was added and the mixture was cooled to -25°. 6-Bromo-5-acenaphthene-methanol (3.7 g, 14 mmol) in toluene (25 ml), warmed to effect solution, was added to the chilled N-chlorosuccinimide-dimethyl sulfide complex. The reaction was stirred at -25° for 3 hr. Triethylamine (2.3 g, 2.5 ml, 30 mmol) was added and the mixture was allowed to warm to room temperature and stand overnight. The reaction was poured into ether (300 ml) and filtered to remove the succinimide. The solution was concentrated to ~ 50 ml, poured into ether and filtered. The ethereal solution was extracted with 1N hydrochloric acid, saturated sodium bicarbonate, and dried over magnesium sulfate. The solvents were removed under reduced pressure and the residue was recrystallized from ethanol. The yield of 6-bromo-5-acenaphthenecarboxaldehyde was 2.05 g (55%), mp 169-172°; ir (KBr, cm$^{-1}$) 1660 (aldehyde C=O), 1600, 1580, 1480, 1435, 1400, 1330, 1200, 1080, 905, 845; nmr (CDCl$_3$, δ) 3.28 (s, 4H, benzylic), 7.03-8.08 (m, 4H, aromatic), 11.5 (s, 1H, CHO); mass spectrum 260,262 (M$^+$).
Anal. Calcd. for C_{15}H_{28}BrO: C, 59.80; H, 3.47.

Found: C, 60.70; H, 3.42.

From combustion and mass spectral data it was determined that the 6-bromo-5-acenaphthenecarboxaldehyde (1\%o) prepared above is a 96.5/3.5 mixture of 1\%o and 5-acenaphthenecarboxaldehyde respectively.

6-Bromo-5-acenaphthenecarboxaldehyde p-Tosylhydrazone (1\%z).

p-Toxylhydrazide (1.3 g, 7 mmol) was added to a solution of 6-bromo-5-acenaphthenecarboxaldehyde (1.65 g, 6.3 mmol) in 95% ethanol (50 ml) and the mixture heated on a water bath until all solids dissolved. Concentrated hydrochloric acid (2 drops) was added and the mixture was cooled to room temperature to effect complete crystallization. Recrystallization from 95% ethanol produced 1.86 g (69\%) of 6-bromo-5-acenaphthenecarboxaldehyde p-tosylhydrazone, mp 203-205° with decomposition; ir (KBr, cm^{-1}) 3300 (NH), 1600, 1370, 1165, 1080, 1030, 960, 890, 840, 810 (aromatic); exact mass: calcd. 428.0194; found 428.0200.

Anal. Calcd for C_{20}H_{17}BrN_{2}O_{2}S: C, 55.95; H, 3.99.

Found: C, 56.48; H, 3.90.
Photolysis of Sodium 6-Bromo-5-acenaphthenecarboxaldehyde p-Tosylhydrazide (144)

6-Bromo-5-acenaphthenecarboxaldehyde p-tosylhydrazone (143, 1.71 g, 4 mmol) was dissolved in anhydrous methylene chloride (250 ml). Excess sodium hydride was washed with pentane and added in several portions until hydrogen evolution ceased. The methylene chloride was removed under reduced pressure, and the resultant solid was suspended in anhydrous ether (180 ml) and irradiated through pyrex with a 450 W Hanovia high pressure mercury arc lamp for 2.5 hr. The mixture was filtered and the solvent removed under reduced pressure to give 840 mg of a reddish-brown residue. The residue was separated by column chromatography into polymeric fractions (mass spectral analysis) which are as yet unidentified.

Thermolysis of Sodium 6-Bromo-5-acenaphthenecarboxaldehyde p-Tosylhydrazide (144)

6-Bromo-5-acenaphthenecarboxaldehyde p-tosylhydrazone (143, 74.7 mg, 1.74 mmol) dissolved in anhydrous methylene chloride (150 ml) was treated with excess sodium hydride until hydrogen evolution ceased. The solution was evaporated to dryness, chlorobenzene (8 ml) was added, and the solution heated at 135° for 45 min. The crude reaction mixture was filtered hot through celite and allowed to cool. Removal of the solvent under reduced pressure yielded 129 mg of a dark tan solid. TLC analysis of the crude reaction
 Ik-3 product revealed the presence of at least nine products. Mass
spectral analysis revealed that no 1-bromo-1,5-dimethylene-1H-
cyclobuta[de]naphthalene (13\textsubscript{ii}) was present, and that the major
components of the mixture were polymeric in nature. The material
was not further characterized.

Acenaphthenequinone Monotosylhydrazone.

Acenaphthenequinone monotosylhydrazone was prepared according
to the method of Cava\textsuperscript{31} in 82\% yield from acenaphthenequinone.

2-Diazo-1-acenaphthenone (8).

2-Diazo-1-acenaphthenone was prepared according to the
method of Cava\textsuperscript{31} in 71\% yield. IR (CH\textsubscript{2}Cl\textsubscript{2}, cm\textsuperscript{-1}) 2100 (N\textsubscript{2}), 1670 (C=O).

Irradiation of 2-Diazo-1-acenaphthenone (8) in Methanol.

A solution of 2-diazo-1-acenaphthenone (97 mg, 0.5 mmol) in
anhydrous methanol (10 mL) was degassed in a stream of nitrogen.
The mixture was irradiated through quartz with a 450 W Hanovia
high pressure mercury arc lamp until nitrogen evolution ceased.
Removal of the methanol under reduced pressure produced 40 mg of
an orange gum which consisted of at least four products (tlc
analysis); ir (KBr, cm\textsuperscript{-1}) 1760, 1740, 1570, 1380, 1000, 775;
exact mass: calcld for C\textsubscript{13}H\textsubscript{10}O\textsubscript{2} 198.0680; found 198.0684; the
fragmentation pattern reveals that this material is not methyl-1H-cyclobuta[de]naphthalene-1-carboxylate (65). The material was not characterized further.
APPENDIX

The Photochemistry of Matrix-isolated
8-Bromo-1-naphthyl diazomethane
Formation of bromide $\text{1}$ from $\text{32}$ is postulated to proceed via photolytic loss of nitrogen to give carbene $\text{34}$, which reacts with the lone-pair electrons on bromine to form bromonium ylid $\text{35}$, which then collapses as in Equation 16.

Recent study$^{38}$ of irradiation of $\text{32}$ in solid argon matrix at low temperature and analysis of the infrared absorption of the product indicates that two intermediates are formed which subsequently collapse to $\text{1}$. 8-Bromo-1-naphthylazomethane (32) was irradiated with light of wavelength greater than 3400 Å, and the progress of the reaction monitored by infrared spectroscopy. The absorption at 2062 cm$^{-1}$, characteristic of the C=N=N asymmetric stretch, was observed to decrease with time while a new set of absorption bands began to appear. The absorptions maximized within a short time, and then these too began to decrease with time as a second new set appeared. These new absorptions increased slowly and gradually leveled off. Continued irradiation at this wavelength failed to produce any significant changes. Irradiation with light greater than 2200 Å, however, caused the third set of absorptions to disappear while absorptions corresponding to $\text{1}$ grew in.

The same photolysis was conducted at 40 K while monitoring with esr spectroscopy. Upon photolysis a free radical signal
appeared which persisted even after extended irradiation with light of wavelength greater than 3400 Å. According to the corresponding times of photolysis and the rates of change of the signals in both the ir and esr experiments, this free radical should be the second observed intermediate. No signals due to a triplet were observed.

The postulated mechanism (Equation 16) is not consistent with the above experimental data. A better mechanism appears to involve formation of bromonium ylid 35 (first intermediate) which upon further irradiation undergoes homolytic cleavage to diradical 146 (second intermediate), which then closes to give 1 (Equation 90).

\[
\begin{align*}
35 & \xrightarrow{\text{hv}} \begin{array}{c}
\text{Br} \\
\text{C-H}
\end{array} & \rightarrow & 1 \\
& \begin{array}{c}
\text{Br} \\
\text{C-H}
\end{array} & \rightarrow & 1
\end{align*}
\]

(90)