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THE SYNTHESIS OF STABLE NAPHTHO[b]Cyclobutadienes

DISSERTATION

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

By

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**********

The Ohio State University
1965

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VITA

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CONTENTS

I INTRODUCTION ................................ 1
II STATEMENT OF PROBLEM .......................... 10
III DISCUSSION AND INTERPRETATION OF RESULTS ...... 13
IV EXPERIMENTAL ................................ 45

a,a'-Bis(phenylethynyl)-o-xylene-a,a'-
diol (34) .............................................. 45

1,2-Dimethoxy-1,2-diphenynaphtho[\(b\)]-
cyclobutene (28) ...................................... 46

1,2-Dichloro-1,2-diphenynaphtho[\(b\)]-
cyclobutene (29) ..................................... 47

Methanolysis of 1,2-Dichloro-1,2-di-
phenynaphtho[\(b\)]cyclobutene (29)
to 1,2-Dimethoxy-1,2-diphenynaphtho-
[\(b\)]cyclobutene (28) .............................. 47

Oxidation of 1,2-Dimethoxy-1,2-diphenyl-
naphtho[\(b\)]cyclobutene (28) to 2,3-
Dibenzoylnaphthalene (47) ......................... 48

Catalytic Reduction of 1,2-Dichloro-1,2-
diphenynaphtho[\(b\)]cyclobutene (29) to
cis-1,2-Diphenynaphtho[\(b\)]cyclo-
butene (49a) ........................................... 48

Pyrolysis of 1,2-Dimethoxy-1,2-di-
phenynaphtho[\(b\)]cyclobutene (28)
to 5-Methoxy-12-phenylnaphthacene (53) ...... 49
CONTENTS (Contd.)

Pyrolysis of 1,2-Dichloro-1,2-diphenyl-
    naphtho[b]cyclobutene (29) to 5-
    Chloro-12-phenynaphthacene (55) .......... 50
Thermal Rearrangement of cis-1,2-Diphenyl-
    naphtho[b]cyclobutene (49a) to 5-phenyl-
    5,12-dihydro naphthacene (56) .............. 50
Isomerization of cis-1,2-Diphenyl-
    naphtho[b]cyclobutene (49a) to trans-1,2-Di-
    phenyl naphtho[b]cyclobutene (49b) .......... 50
N,1,4-Triphenyl-1,2,3,4-tetrahydro-2,3-
    anthracene-dicarboximide (59); cis-
    1,2-Diphenyl naphtho[b]cyclo-
    butene (49a) and N-Phenyl-
    maleimide Adduct ............................. 51
1,3-Diphenyl-1,3-dihydro naphtho[2,3-c]
    thiophene 2,2-dioxide (58) .................. 52
Photolysis of 1,3-Diphenyl-1,3-dihydro-
    naphtho[2,3-c] thiophene 2,2-dioxide (58) .... 52
    to trans-1,2-Diphenyl naphtho[b]-
    cyclobutene (49b) ............................ 52
Aromatization of 5-Phenyl-5,12-dihydro-
    naphthacene (56) to 5-Phenyl-
    naphthacene (60) ............................. 53
<table>
<thead>
<tr>
<th>CONTENTS (Contd.)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of 5-Phenylnaphthacene (60)</td>
<td>53</td>
</tr>
<tr>
<td>1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutadiene (30)</td>
<td>54</td>
</tr>
<tr>
<td>1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutadiene (30) and 2,4,7-Trinitrofluorenone Complex</td>
<td>55</td>
</tr>
<tr>
<td>1,2-Dibromo-1,2-diphenylnaphtho[β]-cyclobutene (65)</td>
<td>56</td>
</tr>
<tr>
<td>Oxidation of 1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutadiene (30) to 2,3-Dibenzoylnaphthalene (47)</td>
<td>56</td>
</tr>
<tr>
<td>Hydrogenation of 1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutadiene (30) to cis-1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutene (49a)</td>
<td>57</td>
</tr>
<tr>
<td>5,5a,11b,12-Tetrahydro-5,5a,11b,12-tetraphenyl-5,12-epoxydibenzo[b, h]biphenylene (66); Adduct of 1,2-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutadiene (30) and 1,4-Diphenyl-2,3-benzofuran (14)</td>
<td>57</td>
</tr>
<tr>
<td>Preparation of 3,8-Diphenyl-1,2-diphenylnaphtho[β]-cyclobutene (21)</td>
<td>58</td>
</tr>
<tr>
<td>1-Bromo-3,8-diphenyl-1,2-diphenylnaphtho[β]-cyclobutene (71)</td>
<td>59</td>
</tr>
<tr>
<td>trans-1,2-Dibromo-3,8-diphenyl-1,2-diphenylnaphtho[β]-cyclobutene (22b)</td>
<td>60</td>
</tr>
</tbody>
</table>
CONTENTS (Contd.)

1,1-Dibromo-3,8-diphenylnaphtho[b]-cyclobutene (72) .................. 60

1,1,2,2-Tetrabromo-3,8-diphenyl-
naphtho[b]cyclobutene (31) ................ 61

Hydrolysis of 1-Bromo-3,8-diphenylnaphtho-
[b]cyclobutene (71) to 1-Hydroxy-3,8-di-
phenylnaphtho[b]cyclobutene (73) .......... 62

Hydrolysis of 1,1-Dibromo-3,8-diphenyl-
naphtho[b]cyclobutene (72) to 3,8-Di-
phenylnaphtho[b]cyclobuten-1-one (74) ...... 62

Oxidation of 1-Hydroxy-3,8-diphenylnaphtho-
[b]cyclobutene (73) to 3,8-Diphenyl-
naphtho[b]cyclobuten-1-one (74) .......... 63

Hydrolysis of 1,2-Dibromo-3,8-diphenyl-
naphtho[b]cyclobutene (22) to 1,2-Di-
hydroxy-3,8-diphenylnaphtho[b]cyclo-
butene (75) ................................ 64

Hydrolysis of 1,1,2,2-Tetrabromo-3,8-
diphenylnaphtho[b]cyclobutene (31)
to 3,8-Diphenylnaphtho[b]cyclo-
butene 1,2-dione (76) ...................... 64

Reduction of 3,8-Diphenylnaphtho[b]cyclo-
butene 1,2-dione (76) with Sodium Borohydrate to 1,2-Dihydroxy-3,8-diphenyl-
naphtho[b]cyclobutene (75) ................. 65

vii
<table>
<thead>
<tr>
<th>CONTENTS (Contd.)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attempted Synthesis of 3,8-Diphenyl-naphtho[b]cyclobutadiene (17)</td>
<td>66</td>
</tr>
<tr>
<td>Trapping of 3,8-Diphenylnaphtho[b]cyclobutadiene (17) with 1,4-Diphenyl-2,3-</td>
<td>66</td>
</tr>
<tr>
<td>benzofuran (14)</td>
<td></td>
</tr>
<tr>
<td>Attempted Synthesis of 1-Bromo-3,8-diphenyl-naphtho[b]cyclobutadiene (77)</td>
<td>67</td>
</tr>
<tr>
<td>Trapping of 1-Bromo-3,8-diphenylnaphtho[b]-cyclobutadiene (77) with 1,4-Diphenyl-</td>
<td>67</td>
</tr>
<tr>
<td>2,3-benzofuran (14)</td>
<td></td>
</tr>
<tr>
<td>1,2-Dibromo-3,8-diphenylnaphtho[b]-cyclobutadiene (32)</td>
<td>68</td>
</tr>
<tr>
<td>Addition of Bromine to 1,2-Dibromo-3,8-diphenylnaphtho[b]cyclobutene (32)</td>
<td>69</td>
</tr>
<tr>
<td>1,2-Dibromo-3,8-diphenylnaphtho[b]cyclobutadiene (32) and 1,4-Diphenyl-2,3-</td>
<td>70</td>
</tr>
<tr>
<td>benzofuran Adduct; 5a,11b-Dibromo-5,6,11,12-tetraphenyl-5,5a,11b,12-</td>
<td></td>
</tr>
<tr>
<td>tetrahydro-5,12-epoxydibenzo[b,h]-biphenylene (79)</td>
<td></td>
</tr>
<tr>
<td>Reaction of 1,2-Dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32) with</td>
<td>70</td>
</tr>
<tr>
<td>Sodium Methoxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CONTENTS (Contd.)</td>
<td>Page</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
</tr>
<tr>
<td>2-Bromo-3,8-diphenyl-naphtho[b]-cyclobuten-1-one (80)</td>
<td>70</td>
</tr>
<tr>
<td>2-Hydroxy-3,8-diphenyl-naphtho[b]-cyclobuten-1-one (81)</td>
<td>71</td>
</tr>
<tr>
<td>APPENDIX I ULTRAVIOLET ABSORPTION SPECTRA</td>
<td>72</td>
</tr>
<tr>
<td>APPENDIX II NUCLEAR MAGNETIC RESONANCE SPECTRA</td>
<td>81</td>
</tr>
<tr>
<td>APPENDIX III INFRARED ABSORPTION SPECTRA</td>
<td>90</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

For years, the chemistry of cyclobutadiene, benzocyclobutadiene, naphthocyclobutadiene and their derivatives has held the interest of many organic chemists. Until the start of this work, all isolable compounds containing a cyclobutadiene nucleus have been either stabilized as their transition metal complexes or fused on both sides as in biphenylene, to aromatic systems.

Among those cyclobutadiene derivatives, which are stabilized by fusion on both sides to aromatic rings, are biphenylene (1) and dibenzobiphenylenes. Biphenylene (1) was first synthesized by Lothrop and 2,3,6,7-dibenzobiphenylene (2) by Curtis and Viswanath. Cava and Stucker synthesized 1,2-benzobiphenylene (3) and 1,2,7,8-dibenzobiphenylene (4), and pointed out that 2,3,6,7-dibenzobiphenylene (2) is thermally more stable than 1,2,7,8-dibenzobiphenylene (4). The stability of these compounds has also

---

been discussed from the theoretical point of view by Ali and Coulson; from molecular orbital calculation of their pi-electron energies and bond orders, it was found that the resonance energy of 2,3,6,7-dibenzobiphenylene (2) exceeds that of 1,2,7,8-dibenzobiphenylene (4) by 4.3 kcal/mol.

\[ (1) \quad (2) \]

\[ (3) \quad (4) \]

---


---

Another group of stabilized cyclobutadiene derivatives are the cyclobutadiene transition metal complexes; examples of the latter include 1,2,3,4-tetramethylcyclobutadiene nickel bromide complex, \(^6,7\) 1,2,3,4-tetraphenylcyclobutadiene nickel bromide complex, \(^8\) 1,2,3,4-tetraphenylcyclobutadiene nickel bromide complex.

---

iron carbonyl complex\textsuperscript{9} or palladium chloride complex\textsuperscript{10} and the recently discovered benzocyclobutadiene iron tricarbonyl complex (5)\textsuperscript{11} etc. These complexes form a group of compounds in which the bonding between the metal and the carbocycle has considerable pi-character.

\begin{align*}
\text{[\includegraphics[width=0.5\textwidth]{complexes.png}]} \\
(5) & \quad (6) & \quad (7)
\end{align*}


A group of stable compounds which may be considered to be closely related to cyclobutadiene are the cyclobutadienoquinones, such as phenylcyclobutadienoquinone (6)\textsuperscript{12} and benzocyclobutadienoquinone (7)\textsuperscript{13} in which all four-membered ring carbons are sp\textsuperscript{2}-hybridized.


In an early study of condensed cyclobutane aromatic systems, Cava and Napier\textsuperscript{14} have shown that zinc dehalogenation
of 1,2-dibromobenzocyclobutene, (8) or the corresponding diiodide gave not the expected benzocyclobutadiene (9), but a dimer. The dehydrobromination of 1,2-dibromobenzocyclobutene (8) with a strong base was also shown to give a product derived from a dimer.$^{15}$ But the presence of benzocyclobutadiene (9) as a transient intermediate was demonstrated by trapping it with active dienes, such as cyclopentadiene,$^{16,17}$ furan$^{17}$ or 1,4-diphenyl-2,3-benzofuran.$^{18}$ A single benzene fused to the system is not enough to stabilize the cyclobutadiene nucleus.

\[ \text{Zn} \rightarrow \begin{array}{c} \text{Dimer} \\ (9) \end{array} \]

\[ (8) \]

\[ \begin{array}{ccc} (10) & (11) & (12) \end{array} \]

\[ 14 \text{ M. P. Cava and D. R. Napier, J. Am. Chem. Soc., 72 1701 (1957).} \]

\[ 15 \text{ M. P. Cava and J. F. Stucker, J. Am. Chem. Soc., 72 1706 (1957).} \]

\[ 16 \text{ C. D. Nenitzescu, M. Avram and D. Dinu, Chem. Ber., 90 2541 (1957).} \]

\[ 17 \text{ M. P. Cava and M. J. Mitchell, J. Am. Chem. Soc., 81 5409 (1959).} \]

\[ 18 \text{ M. P. Cava and R. Pohlke, J. Org. Chem., 27 1564 (1962).} \]
The study of benzocyclobutene chemistry was extended to the synthesis of naphtho[b]cyclobutene (10)\textsuperscript{19} and naphtho[a]-cyclobutene (11)\textsuperscript{20} Since a preliminary attempt to obtain pure 1-bromo, 1,2-dibromo or 1,1,2,2-tetrabromo derivatives of naphtho[b]cyclobutene (10) was not successful, the use of these compounds for the study of hitherto unknown naphtho[b]cyclobutadiene (12) was precluded.


The synthesis of a derivative of naphtho[b]cyclobutadiene was first attempted by Nenitzescu and co-workers\textsuperscript{21,22} The desired naphtho[b]cyclobutadiene derivative was not isolated, but it was trapped as generated by 1,4-diphenyl-2,3-benzofuran to form a Diels-Alder adduct.


In Nenitzescu's first approach via a reverse Diels-Alder reaction, dimethyl tricyclo[4,2,2,0\textsuperscript{2,5}]deca-3,7,9-triene-7,8-dicarboxylate (13), the adduct of cyclooctatetraene and
dimethyl acetylenecarboxylate, was reacted with 1,4-di-phenyl-2,3-benzofuran (14) to give another adduct, namely, dimethyl 1,4,4a,4b,5,10,10a,10b-octahydro-5,10-diphenyl-5,10-epoxy-1,4-ethenobenzoc[b]biphenylene-2,3-dicarboxylate (15), which on dehydration gave dimethyl 1,4,4a,10b-tetrahydro-5,10-diphenyl-1,4-ethenobenzoc[b]biphenylene-2,3-dicarboxylate (16). The thermal decomposition of (16) at 280° gave only polymer. But when the thermal decomposition of (16) was carried out in the presence of 1,4-diphenyl 2,3-benzofuran (14), the Diels-Alder adduct, 5,6,11,12-tetraphenyl-5,5a,11b,12-tetrahydro-5,12-epoxydibenzo[b,h]diphenylene (18), of the intermediate 3,8-diphenynaphthoc[b]cyclobutadiene (17) was obtained in 88% yield.
In Nenitzescu's second approach via a metal dehalogenation reaction, cyclobutene (19), which was generated in situ by the reaction of lithium amalgam on 1,2-dibromocyclobutane, was reacted with 1,4-diphenyl-2,3-benzofuran (14) to give the Diels-Alder adduct, 3,8-diphenyl-2a,3,8,8a-tetrahydro-3,8-epoxynaphtho[b]cyclobutene (20), which on dehydration with acid catalyst gave 3,8-diphenylnaphtho[b]cyclobutene (21) in an overall yield of 30-33%. Bromination of the hydrocarbon (21) with N-bromosuccinimide gave a mixture of bromides, from which 1,2-dibromo-3,8-diphenylnaphtho[b]-cyclobutene (22) was isolated. The dibromo compound (22) was then treated with lithium amalgam to generate the unstable 3,8-diphenylnaphtho[b]cyclobutadiene (17) which was trapped with 1,4-diphenyl-2,3-benzofuran (14) to give the same adduct (18) in 14% yield.
By an alternative method, cis-3,4-dichlorocyclobutene (23) and 1,4-diphenyl-2,3-benzofuran (14) were reacted to give the adduct, 1,2-dichloro-2a,3,8,8a-tetrahydro-3,8-diphenyl-3,8-epoxynaphtho[b]cyclobutene (24), which on acid catalyzed dehydration gave 1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (25). The dichloro compound (25) was then dehalogenated with lithium amalgam in the presence of 1,4-diphenyl-2,3-benzofuran (14) to give the same adduct (18) in 70% yield.

\[ \text{cis-3,4-dichlorocyclobutene (23)} + \text{1,4-diphenyl-2,3-benzofuran (14)} \rightarrow \text{1,2-dichloro-2a,3,8,8a-tetrahydro-3,8-diphenyl-3,8-epoxynaphtho[b]cyclobutene (24)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (25)} \]

\[ \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (25)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (17)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (18)} \]

\[ \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (24)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (26)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (27)} \rightarrow \text{1,2-dichloro-3,8-diphenylnaphtho[b]cyclobutene (21)} \]
If 1,2-dichloro-2a,3,8,8a-tetrahydro-3,8-diphenyl-3,8-epoxynaphtho[b]cyclobutene (24) was dechlorinated with lithium amalgam, 3,8-diphenyl-2a,3,8,8a-tetrahydro-3,8-epoxynaphtho[b]cyclobutadiene (26) was formed, which on catalytic hydrogenation to 2a,3,8,8a-tetrahydro-3,8-diphenyl-3,8-epoxynaphtho[b]cyclobutene (27), followed by acid dehydration gave the hydrocarbon (21).
II. STATEMENT OF PROBLEM

It was the main purpose of this research to synthesize derivatives of naphtho[b]cyclobutadiene which might be stabilized by appropriate substitution especially on the four-membered ring. In another words, the objective of the work was to synthesize derivatives of cyclobutadiene containing only one pair of neighboring carbon fused to an aromatic system, and to attempt to find the minimal substitution necessary for the stability of the naphtho[b]cyclobutadiene system.23

The work was divided into two parts. First the synthesis of a derivative of naphtho[b]cyclobutadiene, which might be stabilized by phenyl groups on the four-membered ring, was investigated. The synthetic approach required the preparation of suitable derivatives of naphtho[b]cyclobutene, namely, 1,2-dimethoxy or 1,2-dichloro-1,2-diphenynaphtho[b]-cyclobutene (28 or 29), by a novel route24 from o-phthalaldehyde and phenylacetylene magnesium bromide in two steps.

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23 A part of the work recorded in this dissertation has been published elsewhere, see ref. 24, 25 and 26.

The 1,2-dichloro compound (29) could conceivably be dehalogenated to the desired 1,2-diphenyl-naphtho[b]cyclobutadiene (30).\textsuperscript{25}

\[
\begin{align*}
\text{OCH}_3 & \quad \text{Cl} \\
\text{OCH}_3 & \quad \text{Cl} \\
\varnothing & \quad \varnothing
\end{align*}
\]

(28) \hspace{1cm} (29) \hspace{1cm} (30)


Second, the synthesis of a 3,8-diphenyl-naphtho[b]cyclobutadiene derivative, which might be stabilized by bromines on the four-membered ring, was planned. The second synthetic approach involved the study of the bromination of the known hydrocarbon, 3,8-diphenyl-naphtho[b]cyclobutene (21), and the debromination and dehydrobromination of the resulting bromo derivatives. For instance, zinc dust debromination of 1,1,2,2-tetrabromo-3,8-diphenyl-naphtho[b]cyclobutene (31)

\[
\begin{align*}
\varnothing & \quad \text{Br} \quad \text{Br} \\
\varnothing & \quad \text{Br} \quad \text{Br} \\
\varnothing & \quad \varnothing
\end{align*}
\]

(31) \hspace{1cm} (32)
should afford 1,2-dibromo-3,8-diphenynaphtho[h]cyclotutadione (32), which might be sufficiently stable to be isolated.

III. DISCUSSION AND INTERPRETATION OF RESULTS

In order to effect the synthesis of the desired derivative of naphtho[b]cyclobutadiene, it was necessary to develop a practical route to a naphtho[b]cyclobutene system. An unusual synthesis of the naphtho[b]cyclobutene ring from a simple benzene derivative was achieved. When a solution of o-phthalaldehyde (33) in ether was reacted with two equivalents of freshly prepared phenylacetylene magnesium bromide, a colorless crystalline product, a,a'-bis(phenylethynyl)-o-xylene-a,a'-diol (34), m. p. 110°, was obtained after hydrolysis, in 70% yield. Its carbon and hydrogen analysis, and infrared absorption spectrum (3.09 µ and 4.47 µ assigned for -OH and C≡C, respectively) are in accord with the structure for the normal Grignard reaction product. The diol (34) was very sensitive to alumina and acids.

\[
\begin{align*}
\text{(33)} & \quad + \quad 2\% \text{-C≡C-MgBr} \\
\rightarrow \\
\text{(34)}
\end{align*}
\]

The chemistry of some acetylenic alcohols has been studied in the last few years. For example, Nagase reported that when diphenylethynyl carbinol (37) was treated with thionyl chloride, 3,4-dichloro-1,2-bis(diphenylmethylene)cyclobutane (39) and 4-chloro-2-(chloromethylene)-1-(diphenylmethylene)-3,3-diphenylcyclobutane (40) were isolated. It was suggested that the four-membered rings were formed by the dimerization of a chloroallene intermediate (38); since it was found by Roedig and Niedenbruck that 3,3-dichloro-1,1-diarylallene (42) (obtained by

\[
\begin{align*}
\text{C} = \text{C} & \rightarrow \text{C} = \text{C} \times \\
& \text{Cl} & \\
\text{(37)} & \text{(38)} & \text{(39)} & \text{(40)}
\end{align*}
\]

\[
\begin{align*}
\text{Ar} \times \text{C} & \rightarrow \text{Ar} \times \\
& \text{C} = \text{C} \times \\
\text{(41)} & \text{(42)} & \text{(43)}
\end{align*}
\]

treatment of 2,3,3-trichloro-1,1-diarylpropene (41) with alcoholic alkali gave a dimer, 3,3,4,4-tetrachloro-1,2-bis-(diaryl)methylene)cyclobutane (43) as it was heated in petroleum ether at 70°. Nagase further reported the same type of dimerization of the allenic intermediate (45) in the reaction of 9-ethynyl-9-fluorenol (44) with thionyl chloride, hydrochloric acid and hydrobromic acid to the corresponding 3,4-dihalo-1,2-difluorenylidene cyclobutane (46).\textsuperscript{32}

\begin{align*}
\text{HO} & \quad \text{C=CH} \\
\rightarrow & \quad \text{HO} \quad \text{C=CH} \\
(44) & \quad (45) \\
\rightarrow & \quad \text{HO} \quad \text{C=CH} \\
\text{HCCl} & \quad \text{HO} \quad \text{C=CH} \\
(45) & \quad (46)
\end{align*}

It was found by Landor and co-workers\textsuperscript{33,34,35} that 1-chloroallenenes could be isolated from the reaction of

\begin{align*}
\text{P. D. Landor and S. R. Landor, Pro. Chem. Soc., 77 (1962).} \\
\end{align*}
certain tertiary acetylenic carbinols with thionyl chloride (Secondary and primary acetylenic alcohols gave mainly the normal acetylenic chlorides).

Since \( a,a'-\text{bis}(\text{phenylethynyl})-\text{o-xylene-}a,a'-\text{diol} \) (34) is a diacetylenic alcohol, it might undergo a similar reaction, upon treatment with a suitable reagent, to give a naphtho[b]cyclobutene derivative. When the diol (34) in a mixture of ether and Skellysolve F was treated with thionyl chloride for a few days at room temperature, a crystalline product was obtained in low yield (8%). The product was assigned the structure 1,2-dichloro-1,2-diphenyl-naphtho[b]-cyclobutene (29), m. p. 149-150° (decomp.), on the basis of some chemical transformations which will be described later.

\[
\begin{align*}
\text{OH} & \quad \text{CH} = \text{C} = \text{C} - \text{OH} \\
\text{CH} = \text{C} = \text{OH} & \quad \text{CH} = \text{C} = \text{C} - \text{CH} = \text{C} = \text{OCH}_3 \\
(34) & \quad (26) \\
\text{CH} = \text{C} = \text{C} - \text{Cl} & \quad \text{Cl} \\
(35) & \quad (29)
\end{align*}
\]
Treatment of the acetylenic alcohol (3+) in ether and Skellysolve F with hydrochloric acid or with hydrogen chloride did not give a crystalline product. But when a solution of the acetylenic alcohol (3+) in methanol was treated with gaseous hydrogen chloride for several minutes, the solution became very hot and upon cooling, a product precipitated out. Recrystallization of the crude product from benzene gave a crystalline compound which was proved to be 1,2-dimethoxy-1,2-diphenylnaphtho[\(b\)]cyclobutene (28), m. p. 150-151\(^\circ\) (decomp.). The yield of this reaction was about 50%. The reaction can be assumed to proceed either via a bischloroallene intermediate, namely, 1,2-bis(3-chloro-3-phenyl-1,2-propadienyl)benzene (35), followed by the formation of 1,2-dichloro-1,2-diphenylnaphtho[\(b\)]cyclobutene (29) and the subsequent solvolysis of (29) to the 1,2-dimethoxy compound (28), or via the formation of a diallenic oxonium ion, namely 2,6-didehydro-4-methyl-3,5-diphenyl-4-benzoninium ion (36), whose geometry is strainless and which contains two allenic systems sitting closely side by side.

In order to later introduce another double bond into the naphtho[\(b\)]cyclobutene system, the 1,2-dimethoxy compound (28), which was obtained in by far the better yield, was converted, in 63% yield, to the 1,2-dichloro compound (29) by an exchange reaction with an excess of acetyl chloride for a few days at room temperature.
The following evidence was obtained in support of the structure of the 1,2-dichloro compound (29) and the 1,2-dimethoxy compound (28). The two chlorine substituents on the four-membered ring of the compound (29) were very easily solvolyzed. On attempted crystallization from methanol, it was converted into the 1,2-dimethyl compound (28) in almost quantitative yield. The ultraviolet spectrum of the 1,2-dimethoxy compound (28) is very similar to that of 2,3-dimethylnaphthalene and naphtho[\(b\)]cyclobutene (10)\(^{19}\) (see Fig.1). The nuclear magnetic resonance spectrum of (28) showed peaks between 7.60 \(\delta\) and 8.23 \(\delta\) corresponding to sixteen aromatic protons, and a single sharp peak at 3.21 \(\delta\) corresponding to six methoxy protons. Reaction of the 1,2-dimethoxy compound (28) with bromine in carbon tetrachloride gave, after work-up, in 60\% yield, 2,3-dibenzoylnaphthalene (47), m. p. 147\(^{\circ}\), which was identical with an authentic sample obtained from the oxidation of 1,2-dihydro-1,3-diphenylnaphtho[2,3-\(\alpha\)]furan-1-ol (48)\(^{36}\) with pyridine-chromium trioxide.

\[\text{(29)} \quad \text{(49a)} \quad \text{cis} \quad \text{(49b)} \quad \text{trans} \quad \text{(50)}\]

The assignment of the naphtho[h]cyclobutene structure was further confirmed by the catalytic reduction of the 1,2-dichloro compound (29) in the presence of palladium-on-charcoal catalyst in benzene-triethylamine solution. Two equivalents of hydrogen was absorbed to give a hydrocarbon which was assigned the structure cis-1,2-diphenylnaphtho[h]-cyclobutene (49a), m. p. 141.5°. Its ultraviolet spectrum was very close to that of 2,3-dimethylnaphthalene and of naphtho[h]cyclobutene (10)¹⁹ (see Fig. 1). The corresponding trans-1,2-diphenylnaphtho[h]cyclobutene (49b) was first synthesized by Van Meter from 2-benzoyl-3-(α-chlorobenzyl)-naphthalene (50)²⁴ with potassium t-butoxide. The stereochemistry of the cis and trans-isomers was assigned on the basis of their nuclear magnetic resonance spectra. Curtin and co-workers,³⁷ who studied the nuclear magnetic resonance spectra of 1,2-diphenylcyclopentanes and cyclopropanes, reported that the isomer exhibiting greater shielding of the aliphatic ring protons is the trans-isomer. Carpino³⁸ also found that the benzylic protons of cis and trans-1,2-di-phenylbenzocyclobutene appear at 5.20 δ and 4.44 δ, respectively. Therefore, in the case of the 1,2-diphenyl-naphtho[h]cyclobutenes (49a and 49b), the isomer with the

more shielded benzylic protons ($\delta = 4.67$) was assigned the trans structure (49b) and the one with less shielded protons ($\delta = 5.29$) was assigned the cis structure (49a) (see Table 1).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-diphenylbenzocyclobutene</td>
<td>$\delta = 5.20$</td>
<td>$4.44$</td>
</tr>
<tr>
<td>1,2-diphenyl[naphtho[b]cyclobutene</td>
<td>$\delta = 5.29$</td>
<td>$4.64$</td>
</tr>
</tbody>
</table>

Integration of the spectrum of the cis-isomer (49a) accounted for sixteen aromatic protons between $\delta = 6.91$ and $\delta = 7.90$, and two benzylic protons.

The stereospecific formation of the cis and trans-1,2-diphenyl[naphtho[b]cyclobutenes (49a and 49b) in the above
reactions may be rationalized. During catalytic reduction, the 1,2-dichloro compound (29) may first form a radical by chlorine abstraction followed by formation of 1,2-diphenyl-naphtho[b]cyclobutadiene (30) as an intermediate which is then hydrogenated in the expected cis manner; on the other hand, the dehydrochlorination of 2-benzyl-3-(a-chlorobenzyl)-naphthalene (50) with potassium t-butoxide may involve formation of an anionic intermediate by abstraction of a benzylic proton followed by the formation of the quinodimethane (57), which then close to give the trans-isomer (49b).

It was observed during the recrystallization of 1,2-dimethoxy-1,2-diphenylnaphtho[b]cyclobutene (28) that when an initially colorless solution of the 1,2-dimethoxy compound (28) in benzene was heated near its boiling point on a steam bath, a yellow or green color developed depending upon the concentration of the solution. If the solution was not heated too long, the color disappeared upon cooling. Though a detailed study of this phenomenon was not made, the observation may indicate that the 1,2-dimethoxy compound (28) is at least partly in equilibrium with the open quinodimethane form, 2,3-dihydro-2,3-bis(a-methoxybenzylidene)naphthalene (51a) which may be relatively stable at 80° without further rearrangement.

When 1,2-dimethoxy-1,2-diphenylnaphtho[b]cyclobutene (28) was heated slightly above its melting point (160-170°),
it was converted into a dark red crystalline product, 5-methoxy-12-phenylnaphthacene (53), m. p. 210-211°, probably via rearrangement to 5,12-dimethoxy-12-phenyl-5,12-dihydronaphthacene (52) followed by the loss of a mole of methanol. In order to effect this cyclization, the syn-form of the naphthoquinodimethane (51a) was probably first formed and then isomerized to the more reactive nonplanar anti-form (51b) which is also stereochemically favorable for ring closure.

![Diagram of chemical structures]

(28) \[ \xrightarrow{\phi} \] (51a) \[ \xrightarrow{\phi} \] (51b)

(28) \[ \xrightarrow{\phi} \] (52) \[ \xrightarrow{\phi} \] (53)

The corresponding 1,2-dichloro-1,2-diphenylnaphtho[b]-cyclobutene (29) also decomposed similarly under the same condition to a red 5-chloro-12-phenylnaphthacene (55), m. p. 180°, presumably via the formation of 5,12-dichloro-12-phenyl-5,12-dihydronaphthacene (54) followed by the loss of hydrogen chloride.
When the aforementioned reaction of 1,2-dimethoxy-1,2-diphenynaphtho[b]cyclobutene (28) with acetyl chloride was performed at a temperature higher than room temperature, a mixture of 5-methoxy-12-phenynaphthacene (53) and 5-chloro-12-phenynaphthacene (55) was obtained instead of the expected 1,2-dichloro-1,2-diphenynaphtho[b]cyclobutene (29).

When a solution of cis-1,2-diphenynaphtho[b]cyclobutene (49a) in N,N-dimethylformamide was refluxed for thirty minutes, an isomer assigned the structure 5-phenyl-5,12-dihydronaphthacene (56), m. p. 150-150.5°, was obtained in 94% yield; this hydrocarbon (56) was identical with the product obtained from trans-1,2-diphenynaphtho[b]cyclobutene (49b) under the same conditions in the same yield.
The rearranged product, 5-phenyl-5,12-dihydronaphthacene (56), was dehydrogenated to the yellow crystalline 5-phenynaphthacene (60), m. p. 193-193.5°, in 50% yield, by heating it with platinum-on-charcoal to about 250° in a salt bath. The dehydrogenated product (60) was identical, in all respects, with an authentic sample obtained by the total synthesis described below.

3-Benzyl-2-naphthoic acid (61)

was treated with thionyl chloride, followed by anhydrous aluminum chloride, to give the intramolecular Friedel-Crafts cyclization product, 5(3H)-naphthacenone (63), m. p. 173-176°, via 3-benzyl-2-naphthoyl chloride (62). The ketone (63) was then reacted with

phenylmagnesium bromide to give 5-phenyl-5,12-dihydro-5-
naphthacenol (64), which without isolation was further treated with hydrochloric acid and dehydrated to the desired yellow 5-phenynaphthacene (60), m. p. 193-193.5°.

The similarity in the ultraviolet spectra of 5-phenynaphthacene (60), 5-methoxy-12-phenynaphthacene (53), and 5-chloro-12-phenynaphthacene (55) supported the structures assigned to the latter two compounds (Fig. 2).

It was found⁴⁰ that the photolytic decomposition of 1,3-diphenyl-1,3-dihydronaphtho[2,3-ε]thiophene 2,2-dioxide (58) gave trans-1,2-diphenynaphtho[1]cyclobutene (49b) probably via the o-quinoid structure (57) by concerted loss of sulfur dioxide, followed by ring closure.

---

The decomposition of sulfone (58) was found to be reversible. When a solution of either cis or trans-1,2-diphenylnaphtho[\(b\)]cyclobutene (49a or 49b) in boiling toluene was treated with sulfur dioxide for twenty minutes, the sulfone, 1,3-diphenyl-1,3-dihydronaphtho[2,3-\(g\)]thiophene 2,2-dioxide (58), m. p. 251°, was obtained in 65% yield. The photolytic decomposition of sulfone (58), which was either obtained from cis or trans-hydrocarbon (49a or 49b), gave only trans-hydrocarbon (49b) in 70% yield. Therefore, this reaction and the rearrangement of cis or trans-hydrocarbon (49a or 49b) to 5-phenyl-5,12-dihydronaphthacene (56) in boiling \(N,N\)-dimethylformamide, and the photolytic decomposition of the sulfone (58) to the trans-hydrocarbon (49b), appear to go through a common intermediate, probably the o-quinodimethane structure (57), which can (a) give trans-hydrocarbon (49b), (b) undergo further rearrangement at higher temperature to the dihydronaphthacene derivative (56), (c) react with sulfur dioxide to give sulfone (58), or (d) react with \(N\)-phenylmaleimide to form the Diels-Alder adduct, \(N,1,4\)-triphenyl-1,2,3,4-tetrahydro-2,3-anthracenedicarboximide (59). Accordingly, one should be able to convert cis-1,2-diphenylnaphtho[\(b\)]cyclobutene (49a), under suitably mild conditions, to its trans-isomer (49b). As expected, it was found that the isomerization can be achieved either photolytically or thermally. The cis-isomer (49a) in
benzene solution was irradiated with ultraviolet light from a Hanovia medium pressure lamp in a quartz probe for forty minutes; after workup, the trans-isomer (49b) was obtained in 60% yield. The cis-isomer (49a) was also converted into its trans-isomer (49b) almost quantitatively, if it was dissolved in toluene and refluxed for about fifteen minutes.

Introduction of a double bond by dehalogenation of a vic-dihalide is usually done by the action of an active metal or metal amalgam. The successful dechlorination of 1,2-dichloro-1,2-diphenynaphtho[b]cyclobutene (29) was achieved by the action of activated zinc dust (the zinc dust was pretreated with saturated ammonium chloride solution, then washed with water, methanol and benzene successively), in boiling benzene for only about two or three minutes. The product, a bright red compound, 1,2-diphenynaphtho[b]cyclobutadiene (30), m. p. 137-138°, was initially separated via formation of its black 2,4,7-trinitrofluorenone complex, m. p. 183°. The reaction mixture of 1,2-dichloro compound (29) and activated zinc dust was treated with activated

![Diagram](image-url)
charcoal and filtered into a solution of 2,3,7-trinitrofluorenone. Upon dilution of the filtrate mixture with ethanol, the black crystalline complex was obtained. The free 1,2-diphenylnaphtho[\textit{b}]cyclobutadiene (30) was regenerated from the complex by chromatography on neutral alumina grade I. It was later found that the hydrocarbon (30) was sufficiently stable to be isolated directly, in 60% yield, by chromatography on alumina, of the crude debrominated product.

The same 1,2-diphenylnaphtho[\textit{b}]cyclobutadiene (30) was obtained, in 46% yield, by the reaction of activated zinc dust on 1,2-dibromo-1,2-diphenylnaphtho[\textit{b}]cyclobutene (65) which was made by the bromination of \textit{trans}-1,2-diphenylnaphtho[\textit{b}]cyclobutene (49b) with N-bromosuccinimide. The assignment of the structure (30) was confirmed by several reactions: (a) addition of bromine, in carbon tetrachloride, to 1,2-dibromo-1,2-diphenylnaphtho[\textit{b}]cyclobutene (65), m. p. 185° (decomp.); (b) its oxidation with either potassium permanganate in acetone or with air while irradiated by ultraviolet light to 2,3-dibenzoylnaphthalene (47); and (c) its catalytic hydrogenation in the presence of palladium-on-charcoal in benzene-ethanol mixture at room temperature in 95% yield to \textit{cis}-1,2-diphenylnaphtho[\textit{b}]cyclobutene (49a).

The naphtho[\textit{b}]cyclobutadiene (30) reacted with 1,4-diphenyl-2,3-benzofuran (14) to form a Diels-Alder adduct,
Generation of the naphtho[b]cyclobutadiene (30) by other reagent such as lithium amalgam at room temperature was tried. Instead of the expected product, a colorless crystalline high melting material, m. p. over 300°, was obtained in 60% yield. The same product, presumably a dimer, was also obtained directly by photolysis of the naphtho[b]cyclobutadiene (30) in benzene with ultraviolet light from a Hanovia medium pressure lamp. The structure of this presumed dimer has not yet been determined. If the reaction of the 1,2-dichloro compound (29) with lithium amalgam was performed under the same conditions in the presence of 1,4-diphenyl-2,3-benzofuran (14) under nitrogen atmosphere, the expected Diels-Alder adduct (66) was obtained in 35% yield.
The stability of 1,2-diphenyl-\( \text{naphtho}[b] \)cyclobutadiene (30) is partly attributed to the fact that the cyclobutadiene ring in (30) is fused to the \( \beta, \beta \)-bond of naphthalene, a position of low pi-bond order. This should reduce the cyclobutadienoid character of the four-membered ring by increasing the single bond character or reducing the pi-bond character of 2a,8a-bond. This is parallel to the fact that dimethylenecyclobutenes\(^4\) are stable. Nuclear magnetic resonance data of 1,2-diphenyl-\( \text{naphtho}[b] \)cyclobutadiene (30) also indicated that bonds between C-2a and C-3, and between C-8 and C-8a have considerable double bond character. In addition to fourteen protons in the usual aromatic region (between \( \delta = 7.18 \) and \( \delta = 7.71 \)), two protons appeared as a sharp peak at 6.50 \( \delta \); the position of these protons at C-3 and C-8 is very near to that of the olefinic protons (6.55 \( \delta \)) of cis-stilbene.


The two phenyl groups at C-1 and C-2 positions may partly contribute to the stability of the cyclobutadiene system by conjugation. Freedmann\(^5\) attempted to synthesize 1,2,3,4-tetraphenylcyclobutadiene, which should be stabilized.

by similar effect, although he found that it was not sufficiently stable to permit isolation. Molecular orbital calculations of 1,2-diphenyl-naphtho[b]cyclobutadiene (30) and related compounds by Anastassiou and Coulson, et al. indicate that the four-membered ring residue in the naphtho[b]-cyclobutadiene (30) is a trapezoidal structure and that the extent of double bond fixation for C-2a to C-3 and C-8 to C-8a links is quite abnormally high. This result agrees with the assignment of the highest field signal in the nuclear magnetic resonance spectrum to the protons at C-3 and C-8, and also parallels the prediction that cyclobutadiene is calculated not to be stable in a totally aromatic square configuration and tend to distort in such a way as to favor one of the two possible rectangular Kekulé structures.


After having found that 1,2-diphenyl-naphtho[b]cyclobutadiene (30) is stable, it was of interest to try to synthesize a naphtho[b]cyclobutadiene without phenyl substituents on the four-membered ring, and to examine the possible stabilizing effect of another substituent, such as bromine, on the
four-membered ring. The use of the unsubstituted naphtho[\textsubscript{b}]-cyclobutene (10) as starting material for this study was temporarily excluded, because earlier attempts by Shirley\textsuperscript{19} to obtain pure mono, dibromo or tetrabromo derivatives of (10) were unsuccessful; therefore, 3,8-diphenylnaphtho[\textsubscript{b}]-cyclobutene (21) was chosen as the starting material. As discussed in the earlier part of this dissertation, Nenitzescu and co-workers\textsuperscript{21,22} failed to isolate 3,8-diphenylnaphtho[\textsubscript{b}]cyclobutadiene (17) from the dehalogenation of 1,2-dihalo-3,8-diphenylnaphtho[\textsubscript{b}]cyclobutenes (22 and 24). It was of interest, therefore, to attempt the synthesis of 1-bromo-3,8-diphenylnaphtho[\textsubscript{b}]cyclobutadiene (78) and 1,2-dibromo-3,8-diphenylnaphtho[\textsubscript{b}]cyclobutadiene (32).

In the original synthesis of 3,8-diphenylnaphtho[\textsubscript{b}]-cyclobutene (21), both of which are difficult to prepare, were used as starting materials. For this reason, a much more convenient synthesis of 3,8-diphenylnaphtho[\textsubscript{b}]cyclobutene (21) was employed in the work described here. The improved synthesis\textsuperscript{46} involved refluxing a mixture of 1,4-diphenyl-2,3-benzofuran (14) with an excess of 3-sulfolene (67) in benzene, followed by acid catalyzed dehydration of the Diels-Alder adduct, 4,9-diphenyl-4,9-epoxy-1,3,4,9-tetrahydronaphtho[2,3-\textsubscript{g}]thiophene 2,2-dioxide (68) to 4,9-diphenyl-1,3-dihydronaphtho[2,3-\textsubscript{g}]thiophene 2,2-dioxide (69),

\textsuperscript{46} J. P. Van Meter, Ph. D. dissertation, The Ohio State University.
and final pyrolytic decomposition of the sulfone (69) to the desired hydrocarbon (21).

\[
\begin{align*}
&\text{(14)} \quad + \quad \text{(67)} \quad \rightarrow \quad \text{(68)} \\
&\text{(68)} \quad \rightarrow \quad \text{(69)} \quad \rightarrow \quad \text{(21)}
\end{align*}
\]

Bromination of the hydrocarbon (21) with N-bromosuccinimide in carbon tetrachloride under the catalytic influence of dibenzoyl peroxide gave, depending upon the reaction conditions, all of the possible bromination products (or mixtures of these compounds) except \(1,1,2\)-tribromo-\(3,8\)-diphenylnaphtho\([b]\)cyclobutene (70) and \(\text{cis-1,2-dibromo-3,8-diphenylnaphtho}[b]\)cyclobutene (22a). Reaction of the hydrocarbon (21) with one equivalent of \(N\)-bromosuccinimide in refluxing carbon tetrachloride for thirty minutes, in the presence of dibenzoyl peroxide, gave 1-bromo-\(3,8\)-diphenylnaphtho\([b]\)cyclobutene (71), m. p. 143-144°, in 36% yield. When two equivalents of \(N\)-bromosuccinimide were used under the same conditions, \(\text{trans-1,2-dibromo-3,8-diphenylnaphtho}\)[\(b\)]cyclobutene (22b), m. p. 198.5°; was isolated in 48%
yield; in addition, some 1,1-dibromo-3,8-diphenynaphtho[12]cyclobutene (72), m. p. 174-175°, was isolated from the mother liquor. In another experiment, when three equivalents of N-bromosuccinimide was used, the 1,1-dibromo compound (72) was obtained in 31% yield, in addition to the trans-1,2-dibromo compound (22b) which was produced in about 17% yield; but no tribromo compound (70) was isolated. When the bromination was performed under slightly different conditions by changing such variables as the amount of the reagent and the catalyst or the time of reaction, etc., it was found that unless considerable amount of dibenzoyl peroxide was used, only dibromo compounds were formed, even when more than four equivalents of bromination agents were used. But in the presence of a large amount of catalyst, hydrocarbon (21) can
be brominated, using six to eight equivalents of the reagent, to 1,1,2,2-tetrabromo-3,8-diphenylnaphtho[b]cyclobutene (31), m. p. 222-223°, in 32% yield.

The structure assigned to these bromo compounds were supported by their elementary analysis and their reactions with silver trifluoroacetate, followed by water. The monobromo compound (71) was thus converted to 1-hydroxy-3,8-diphenylnaphtho[b]cyclobutene (73), m. p. 206-207°, which was then oxidized by chromium trioxide to 3,8-diphenylnaphtho[b]-cyclobuten-1-one (74), m. p. 205°. The ketone (74) was also obtained from the hydrolysis of the 1,1-dibromo compound (72). The trans-1,2-dibromo compound (22b) was converted into the
corresponding hydroxy compound, 1,2-dihydroxy-3,8-diphenyl-
naphtho[\(b\)]cyclobutene (75), m. p. 200-205°. Hydrolysis of 4,1,2,2-tetrabromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (31) gave the expected diketone, 3,8-diphenylnaphtho[\(b\)]cyclobutene 1,2-dione (76), double m. p. 238° and 238°, which upon sodium borohydride reduction gave the identical 1,2-dihydroxy-3,8-diphenylnaphtho[\(b\)]cyclobutene (75).

\[
\begin{align*}
\text{(31)} & \quad \rightarrow \quad \text{(76)} & \quad \rightarrow \quad \text{(75)}
\end{align*}
\]

The assignment of the trans-configuration to the 1,2-dibromo compound (22) was based upon a comparison of nuclear magnetic resonance spectra of the bromo derivatives of 3,8-diphenylnaphtho[\(b\)]cyclobutene with those of benzocyclobutene.\(^{47}\)


The \(\delta\)-values of the benzylic protons for these compounds are given in Table 2. It was found that these protons in the 3,8-diphenylnaphtho[\(b\)]cyclobutenes appeared at about 0.12 to 0.21 ppm to lower fields than in the corresponding benzo-
cyclobutene. The 1,2-dibromo-3,8-diphenylnaphtho[\(b\)]cyclo-
butene (22) obtained here showed benzylic protons at \(\delta = 5.54,\)
Table 2

\[
\begin{align*}
\text{H(1)} & \quad \text{H(1)} & \quad 3.14 = \delta_1 = 3.23 \\
\text{H(1)} & \quad \text{H(1)} \\
\text{H(1)} & \quad \text{H(1)} \\
\text{Br} & \quad \text{H(1)} & \quad 5.31 = \delta_1 = 5.46 \\
\text{H(2)} & \quad \text{H(2)} & \quad 3.78 = \delta_2 = 3.80 \\
\text{H(3)} & \quad \text{H(3)} & \quad 3.41 = \delta_3 = 3.62 \\
\text{Br} & \quad \text{Br} & \quad 5.81 = \delta_1 = \ldots \\
\text{Br} & \quad \text{Br} \\
\text{H(1)} & \quad \text{H(1)} & \quad 5.41 = \delta_1 = 5.54 \\
\text{Br} & \quad \text{Br} & \quad 5.41 = \delta_2 = 5.54 \\
\text{Br} & \quad \text{Br} & \quad ---- = \delta_1 = 4.37 \\
\text{H(1)} & \quad \text{H(1)} & \quad ---- = \delta_2 = 4.37 \\
\end{align*}
\]
beside aromatic protons in the usual region. The value $\delta = 5.54$ is only 0.13 ppm to lower field than the value $\delta = 5.41$ previously reported$^{47}$ for the benzylic protons of trans-1,2-dibromobenzocyclobutene. Other data in Table 2 also support the structures assigned to the 1-bromo and 1,1-dibromo derivatives of 3,8-diphenynaphtho[b]cyclobutene (71 and 72).

The stereochemistry of 1,2-dihydroxy-3,8-diphenynaphtho[b]cyclobutene (75) was not determined; it was prepared merely for the correlation of the structures of 1,2-dibromo-3,8-diphenynaphtho[b]cyclobutene (22), 1,1,2,2-tetrabromo-naphtho[b]cyclobutene (31) and 3,8-diphenynaphtho[b]cyclobutene 1,2-dione (76).

The attempted synthesis of the hitherto unknown 3,8-diphenynaphtho[b]cyclobutadiene (17) by either dehydrobromination of 1-bromo-3,8-diphenynaphtho[b]cyclobutene (71) with potassium t-butoxide or debromination of 1,2-dibromo-3,8-diphenynaphtho[b]cyclobutene (22) with activated zinc dust resulted only in the formation of polymeric material. In accord with the earlier report,$^{22}$ the cyclobutadiene (17) was trapped by 1,4-diphenyl-2,3-benzofuran (14) to give a Diels-Alder adduct (18), m. p. 259°. Similarly, 1-bromo-3,8-diphenynaphtho[b]cyclobutadiene (77) was not isolated, when either 1,1-dibromo-3,8-diphenynaphtho[b]cyclobutene (72) or trans-1,2-dibromo-3,8-diphenynaphtho[b]cyclobutene (22b) was treated with potassium t-butoxide; the initial
generation of the bromocyclobutadiene (77) was demonstrated, however, by trapping it with 1,4-diphenyl-2,3-benzofuran (14) to give a Diels-Alder adduct, 11b-bromo-5,6,11,12-tetraphenyl-5,5a,11b,12-tetrahydro-5,12-epoxydibenzo[h,h]biphenylene (78), m. p. 276.5°. In contrast, the treatment of 1,1,2,2-tetrabromo-3,8-diphenynaphtho[b]cyclobutene (31) with activated zinc dust for ten to fifteen seconds in boiling benzene solution afforded, in 40% yield, a stable orangelow yellow crystalline compound, 1,2-dibromo-3,8-diphenynaphtho[b]cyclobutadiene (32), m. p. 162-169° (decomp.). Treatment of this compound with bromine in carbon tetrachloride gave back the original tetrabromo compound (31) in good yield.

(22b) or (72) → (77) → (78)

(31) → (32) → (79)
The dibromocyclobutadiene (32) reacted readily in benzene with 1,4-diphenyl-2,3-benzofuran (14) to form, in excellent yield, the expected Diels-Alder adduct, 5a,11b-dibromo-5,6-11,12-tetraphenyl-5,5a,11b,12-tetrahydro-5,12-epoxydibenzoc[b,h]diphenylene (79), m. p. 320°; and catalytic reduction of (32) in the presence of palladium-on-charcoal and triethylamine gave hydrocarbon (21) in low yield.

In order to examine the stability of the dibromocyclobutadiene (32) to a strong base, it was treated with freshly prepared sodium methoxide in methanol under nitrogen atmosphere. After the usual workup, a yellow crystalline product was isolated. This compound, which was isolated in 60% yield, was identified as 2-bromo-3,8-diphenyl[2,3]naphtho[2,1-cyclobuten-1-one (80), m. p. 190-191°; it showed strong carbonyl absorption in the infrared spectrum at 5.6 μ. The assignment of the structure (80) was supported by its synthesis from 3,8-diphenyl[2,3]naphtho[2,1-cyclobuten-1-one (74). Bromination of the ketone (74) with one equivalent of N-bromosuccinimide in the presence of dibenzoyl peroxide in carbon tetrachloride afforded bromoketone (80) in 60% yield.
Reduction of 3,8-diphenylnaphtho[b]cyclobuten-1,2-dione (76) under mild conditions with zinc dust and ammonium chloride in benzene and dioxane afforded a pale yellow compound, 2-hydroxy-3,8-diphenylnaphtho[b]cyclobuten-1-one (81), m. p. 226°, in about 50% yield; the same hydroxy ketone (81) was obtained from the reaction of bromoketone (80) with silver trifluoroacetate in benzene, followed by treatment with water. The hydroxyketone (81) showed strong carbonyl absorption at 5.7 μ and strong hydroxy absorption at 2.90 μ in its infrared spectrum. The strong carbonyl bands in the spectra of the bromoketone (80), monoketone (74) and hydroxyketone (81) indicated that they do not spontaneously enolize to the corresponding enol forms, or cyclobutadienoid tautomers (82, 83 and 84).
From these results, it may be concluded that the stability of 1,2-dibromo-3,8-diphenylmnaptho[b]cyclobutadiene (32) is attributable, in part, to the two bromine substituents, presumably due to the electronegativity of bromines which withdraw electrons inductively from the system to reduce the pi-bond order of the 1,2-bond. One bromine substituent on the four-membered ring seems to be insufficient to stabilize the naphtho[b]cyclobutadiene system.

The two phenyl substituents at C-3 and C-8 probably add little resonance stabilization to the naphtho[b]cyclobutadiene system, since as in 1-phenynaphthalene, they must be twisted considerable out of the plane of the naphthalene ring.

According to simple molecular orbital theory, cyclobutadiene, with four pi-electrons, does not meet the requirement for stability according to Hückel's rule. The four sigma-bonds are bent and pi-electrons tend to be localized either as two non-conjugated double bonds in a rectangular form or in the next higher electronic state as a triplet in a square diradical form.48


In the earlier part of this discussion, it has been pointed out that in 1,2-diphenylmnaptho[b]cyclobutadiene (30)
the degree of double bond fixation between C-2a and C-3 and between C-8 and C-8a bonds is so high that there is relatively little double bond character in the C-2a to C-8a bond. This should be the same in the case of 1,2-dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32). But in the former case, the double bond between C-1 and C-2 is stabilized by the resonance effect of the two phenyl groups at C-1 and C-2. In the latter case, the double bond between C-1 and C-2 may be stabilized by the inductive effect of the two bromines which reduce the free valence indices at these positions.

Both phenyl and bromine substituents may also stabilize the cyclobutadiene system by steric hindrance which reduces the reactivity at carbon atoms 1 and 2.

1,2-Diphenyl-naphtho[b]cyclobutadiene (30) and 1,2-dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32) represent the only known examples of isolable compounds containing
a cyclobutadiene nucleus which are not metal complexed and which have only one pair of neighboring carbons fused to an aromatic system. The presence of suitable substituents on the unfused side of the four-membered ring also contributes greatly to the stability of the cyclobutadiene system in these compounds.
IV. EXPERIMENTAL

All melting points are uncorrected. Microanalyses were done by Alfred Bernhardt, Max-Planck Institute, Mülheim, Germany; Midwest Microlab. Inc., Indianapolis, Indiana and Schwartzkopf Laboratories, Woodside, New York.

\(a,a'-\text{Bis(phenylethynyl)-o-xylene-}\alpha,\alpha'-\text{diol (34)}\). — A solution of phenylethynylmagnesium bromide was prepared in a 250 ml. round bottomed flask by adding dropwise a solution of 5.1 g. of phenylacetylene in 25 ml. of dry ether to a solution of 3M ethylmagnesium bromide (17 ml.). After the mixture was warmed for 30 minutes to complete the reaction, a solution of 3.4 g. of phthalaldehyde in 100 ml. of dry ether was added over a period of 30 minutes and the mixture was stirred for 5 hours. The reaction mixture was then decomposed with 100 ml. of 5% ammonium chloride in water in the usual manner. The ether layer was separated and the aqueous layer extracted with 50 ml. of ether. The combined ether extracts was dried over magnesium sulfate for 30 minutes. After evaporation of the solvent ether, the residual oil was crystallized from benzene-Skellysolve F mixture. Colorless crystalline needle product (6 g.), m. p. 110°, was obtained. The presence of hydroxy group and acetylenic linkage was confirmed by the infrared absorption at 3.09 and 4.47 μ respectively.
Anal. Calcd. for $C_{24}H_{18}O_2$ : C, 85.18; H, 5.36.

Found : C, 84.81; H, 5.23.

1,2-Dimethoxy-1,2-diphenynaphtho[blcyclobutene (28).--

$\alpha,\alpha'$-Bis(phenylethynyl)-o-xylene-$\alpha,\alpha'$-diol (34), 3 g., was dissolved in 30 ml. of absolute methanol. Dry hydrogen chloride was then passed through the solution until the solution became hot and saturated with hydrogen chloride. The reaction mixture was diluted with 30 ml. of methanol and stirred. The product, which crystallized upon cooling to room temperature was obtained by filtration. The filtrate, after being treated with 2.5 g. of activated charcoal, was concentrated to about 45 ml. More product crystallized out upon cooling. The combined crude product (2.0 g.) was re-crystallized from benzene-cyclohexane mixture or acetone-methanol mixture to give 1.5 g. of pure colorless crystalline product, m. p. 150-151° (decomp.). It was observed that benzene solution of the colorless product at the boiling point of benzene turned yellow or green depending upon the concentration. Upon cooling, the colored solution turned back to colorless. The ultraviolet spectrum of the product showed the following maxima (in ethanol):

$\lambda_{\text{max}}$ 230 μ (log $e$ = 4.98), 261(3.67), 271(3.74), 282(3.75), 298(3.61), 306(3.13), 312(2.87), 319(3.18).

Anal. Calcd. for $C_{26}H_{22}O_2$ : C, 85.21; H, 6.05.

Found : C, 85.16; H, 5.97.
1,2-Dichloro-1,2-diphenyl-11aphtho[b]cyclobutene (29). — (a) 1,2-Dimethoxy-1,2-diphenyl-11aphtho[b]cyclobutene (28), 3 g, was dissolved in 100 ml. of acetyl chloride at room temperature and the solution was kept for 50 hours in a flask with drying tube. The colorless crystal, which formed in the flask, was obtained by filtration. Additional product was obtained from the filtrate upon evaporation of acetyl chloride under reduced pressure. Recrystallization of the combined product (2 g.) from benzene-ether mixture gave colorless crystalline product, 1,2-dichloro-1,2-diphenyl-11aphtho[b]cyclobutene (29), m. p. 149-150° (decomp.).

Anal. Calcd. for C_{24}H_{16}Cl_{2}: C, 76.81; H, 4.26; Cl, 18.90.

Found : C, 76.73; H, 4.41; Cl, 18.93.

(b) a,a'-Bis(phenylethynyl)-o-xylene-a,a'-diol (34), 5 g., was dissolved in 30 ml. of dry ether, 30 ml. of Skellysolve F and 5 g. of thionyl chloride at room temperature. The solution was kept for 80 hours. The colorless crystals, which formed in the flask were separated by filtration and recrystallized from benzene-ether mixture. The product was identical with the one obtained by Method (a). But the yield was low (0.5 g.). No more product was isolated from the filtrate from the reaction mixture.

Methanolysis of 1,2-Dichloro-1,2-diphenyl-11aphtho[b]cyclobutene (29) to 1,2-Dimethoxy-1,2-diphenyl-11aphtho[b]cyclobutene (28). — 1,2-Dichloro-1,2-diphenyl-11aphtho[b]cyclobutene (29), 100 mg., was dissolved in about 1 ml. of acetone and 4 ml. of
methanol and heated on a steam bath for about 20 minutes. The solution was concentrated to about 2 ml. and was then diluted with 1 ml. of methanol and cooled. The colorless crystalline product, obtained in 90% yield, was identical with 1,2-dimethoxy-1,2-diphenyl-naphtho[b]cyclobutene (28), m. p. 150-151°.

Oxidation of 1,2-Dimethoxy-1,2-diphenyl-naphtho[b]cyclobutene (28) to 2,3-Dibenzoylnaphthalene (47). — To a solution of 1,2-dimethoxy-1,2-diphenyl-naphtho[b]cyclobutene (28), 0.80 g., in 30 ml. of carbon tetrachloride was added 2 g. of bromine in 10 ml. of carbon tetrachloride. After an hour at room temperature, deep red crystals formed which was filtered. The red crystals decolorized slowly to pale yellow. From the mother liquor or recrystallization of the red crystals, the same colorless crystals were obtained. The combined product, after being recrystallized from ether-Skellysolve F mixture, weighed 0.48 g., m. p. 146°. This was identical with an authentic sample of 2,3-dibenzoylnaphthalene (47). Their infrared spectra were identical and mixed melting point was not depressed.

Catalytic Reduction of 1,2-Dichloro-1,2-diphenyl-naphtho-b[cyclobutene (29) to cis-1,2-diphenyl-naphtho-b[cyclobutene (49a). — A solution of 1,2-dichloro-1,2-diphenyl-naphtho[b]cyclobutene (29), 0.1810 mg., in 25 ml. of benzene and 25 ml. of triethylamine, was hydrogenated under the
catalytic influence of palladium-on-charcoal (100 mg.) at room temperature (275 K) and under atmospheric pressure (744.6 mm.). Hydrogen absorbed was 29.1 ml. equivalent to 2.14 mol. calculated from the amount of starting material. The reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was chromatographed with benzene over neutral alumina grade I. Upon evaporation of the eluant, colorless crystalline cis-1,2-diphenylnaphtho[b]cyclobutene (49a), m. p. 1^{141.5} \degree, was obtained in 90\% yield; ultraviolet spectrum : \lambda_{\text{max}} 225 \text{ m}\mu (\log e = 4.48), 261(3.55), 270(3.63), 280(3.65), 292(3.52), 305(3.04), 306(2.80), 312(2.84), 319(3.21).

**Anal. Calcd. for C_{24}H_{18}**:
- C, 94.08; H, 5.92.
- Found : C, 93.99; H, 5.86.

**Pyrolysis of 1,2-Dimethoxy-1,2-diphenylnaphtho[b]cyclobutene (28) to 5-Methoxy-12-phenylnaphthacene (53).** — 1,2-Dimethoxy-1,2-diphenylnaphtho[b]cyclobutene (28), 0.5 g., was placed in a Pyrex test tube and was heated at 160-170\degree in a salt bath for three minutes. The resulting red melt was cooled to room temperature and washed with minimum amount of acetone. Recrystallization of the red product from acetone and then from benzene-cyclohexane mixture gave analytical sample of 5-methoxy-12-phenylnaphthacene (53), 0.35 g., m. p. 210-211\degree.

**Anal. Calcd for C_{24}H_{18}O**:
- C, 89.79; H, 5.43.
- Found : C, 89.87; H, 5.45.
Pyrolysis of 1,2-Dichloro-1,2-diphenynaphtho[b]cyclobutene (29) to 5-Chloro-12-phenynaphthacene (55). -- One gram of 1,2-dichloro-1,2-diphenynaphtho[b]cyclobutene (29) was placed in a Pyrex test tube and was heated to melt at 160-170° in a salt bath for one minute. The red melt solidified as it cooled to room temperature. Recrystallization of the red solid from benzene-ether mixture gave pure 5-chloro-12-phenynaphthacene (55), 0.9 g., m. p. 180°.

Anal. Calcd for C_{24}H_{15}Cl: C, 85.09; H, 4.46; Cl, 10.46.
Found: C, 84.91; H, 4.59; Cl, 10.43.

Thermal Rearrangement of cis-1,2-Diphenylnaphtho[b]-cyclobutene (49a) to 5-Phenylo-5,12-dihydronaphthacene (56). -- A solution of cis-1,2-diphenylnaphtho[b]cyclobutene (49a), 265 mg., in N,N-dimethylformamide (10 ml.) was refluxed for 30 minutes. The solvent was then evaporated to dryness in a rotary evaporator under reduced pressure. The residue was then taken up by small amount of benzene and chromatographed over neutral alumina grade I. After evaporation of benzene from the eluant, 250 mg. of 5-phenyl-5,12-dihydronaphthacene (56), m. p. 150-150.5°, was obtained, which was identical with the authentic sample prepared from trans-1,2-diphenynaphtho[b]cyclobutene (49b).

Isomerization of cis-1,2-Diphenylnaphtho[b]cyclobutene (49a) to trans-1,2-Diphenylnaphtho[b]cyclobutene (49b). -- (a) Photolytic isomerization -- cis-1,2-Diphenylnaphtho[b]-cyclobutene (49a) was dissolved in 250 ml. of benzene and
irradiated with ultraviolet light from a Hanovia medium pressure lamp in a quartz probe for 40 minutes. After evaporation of benzene, and recrystallization of the residue from benzene-ether mixture, 60 mg. of trans-1,2-diphenynaphtho[b]cyclobutene (49b), m. p. 157.5°, identical with the authentic sample; was obtained.

(b) Thermal isomerization — cis-1,2-Diphenynaphtho[b]cyclobutene (49a), 50 mg., was dissolved in 5 ml. of toluene and refluxed for 15 minutes. Evaporation of solvent gave 45 mg. of trans-1,2-diphenynaphtho[b]cyclobutene (49b).

K,1,b-Triphenyl-1,2,1,b-tetrahydro-2,1-anthracene-dicarboximide (59); cis-1,2-Diphenynaphtho[b]cyclobutene (49a) and N-Phenylmaleimide Adduct. — cis-1,2-Diphenynaphtho[b]cyclobutene (49a), 800 mg., and N-phenylmaleimide, 200 mg., were mixed thoroughly and placed in a Pyrex test tube. The mixture was then heated at 170-175° in a salt bath for 10 minutes. After cooling to room temperature, the solid material was dissolved in 6 ml. of methylene chloride and chromatographed over neutral alumina grade III. The eluant was evaporated to dryness under reduced pressure and the residue recrystallized from methylene chloride twice, and from benzene-cyclohexane mixture twice. The recrystallized product, weighed 105 mg., m. p. 279°, was identical with the adduct of trans-1,2-diphenynaphtho[b]cyclobutene (49b) and N-phenylmaleimide.
1,3-Diphenyl-1,3-dihydronaphtho[2,3-c]thiophene 2,2-dioxide (58). -- A solution of cis-1,2-diphenylnaphtho[b]-cyclobutene (49a), 140 mg., in 50 ml. of toluene was heated to boil and was treated with a stream of gaseous sulfur dioxide for 20 minutes. The solution immediately turned pink and gradually became yellow. The reaction mixture was cooled to room temperature and evaporated to dryness in a rotary evaporator under reduced pressure. The yellow residue was recrystallized twice from benzene-Skellysolve F mixture to give colorless crystalline product, 110 mg., m. p. 251° (decomp.).

Anal. Calcd. for C_{24}H_{18}S_{2}: C, 77.80; H, 4.90; S, 8.65.
Found: C, 78.11; H, 5.24; S, 8.37.

The same result was obtained, when trans-1,2-diphenyl-naphtho[b]cyclobutene (49b) was used.

Photolysis of 1,3-Diphenyl-1,3-dihydronaphtho[2,3-c]-thiophene 2,2-dioxide (58) to trans-1,2-Diphenylnaphtho[b]-cyclobutene (49b). -- A solution of 220 mg. of 1,3-diphenyl-1,3-dihydronaphtho[2,3-c]thiophene 2,2-dioxide (58) in 200 ml. of benzene was irradiated in a quartz probe with ultraviolet light from a Hanivvia medium pressure lamp for an hour under nitrogen atmosphere. The solution was then evaporated to dryness under reduced pressure and the residue was chromatographed over neutral alumina grade I with benzene. trans-1,2-Diphenylnaphtho[b]cyclobutene (49b), m. p. 157.5°,
was obtained, in 70% yield, upon evaporation of the eluant.

Aromatization of 5-Phenyl-5,12-dihydronaphthacene (56) to 5-Phenylnaphthacene (60). — 5-Phenyl-5,12-dihydronaphthacene (56), 160 mg., and 5% platinum-on-charcoal 295 mg., were mixed throughly and placed in a Pyrex test tube. The mixture was then heated at 240-250° in a salt bath for 15 minutes. After cooling, 2 ml. of benzene was added to dissolve the product and platinum-on-charcoal was removed by filtration. Upon evaporation of the filtrate, 75 mg. of yellow crystalline 5-phenylnaphthacene (60) was obtained. Recrystallization of the product from benzene-Skellysolve F mixture gave the analytical sample, m. p. 193-193.5°.

Anal. Calcd. for C_{24}H_{16}: C, 94.70; H, 5.30.

Found: C, 94.36; H, 5.55.

Synthesis of 5-Phenylnaphthacene (60). — A solution of 2 g. of 3-benzyl-2-naphthoic acid (61) in 50 ml. of benzene was mixed with 5 ml. of thionyl chloride. After 20 minutes of heating on a steam bath, the solvent benzene and excess of thionyl chloride were evaporated to dryness in a rotary evaporator under reduced pressure. The residual oil consisting mainly of 3-benzyl-2-naphthoyl chloride (62) was dissolved in 100 ml. of methylene chloride and cooled to 0° in a ice bath. Aluminum chloride, 2 g., was then added in small portions with stirring to the solution. The resulting mixture was stirred for an hour, and it was then poured
slowly into a cold solution of dilute hydrochloric acid (100 ml.). The aqueous solution was then extracted three times with 50 ml. of methylene chloride, and the combined extracts were dried over anhydrous calcium chloride. The dried extract was evaporated to dryness. Recrystallization of the residue from acetone gave 0.51 g. of 5(2H)-naphthacenone (63), m. p. 173-176°.

5(2H)-Naphthacenone (63), 0.5 g., was dissolved in 50 ml. of benzene and equal mole of phenylmagnesium chloride solution (0.7 ml., 3M) was added dropwise with stirring. After an hour of stirring at room temperature, the reaction mixture was treated with an aqueous solution of ammonium chloride and was extracted with two 15 ml. portions of benzene, followed by two 15 ml. portions of ether. The combined extracts were evaporated to dryness. The oily residue consisting mainly of 5-phenyl-5,12-dihydronaphthacenol (64) was dissolved in 30 ml. of methanol. Hydrochloric acid (6N) was then added dropwise to the methanolic solution with stirring until no further precipitate formed. The yellow precipitate was separated by filtration and recrystallized from benzene-Skellysolve F mixture to give 0.3 g. of yellow crystals, m. p. 193°, which was identical with the 5-phenylnaphthacene (59) obtained above.

1,2-Diphenylnaphtho[b]cyclobutadiene (30). — To a hot solution of 100 mg. of 1,2-dichloro-1,2-diphenylnaphtho[b]-cyclobutene (29) was added 2.5 g. of zinc dust previously
activated by washing with saturated ammonium chloride solution, followed by rinsing with water, alcohol and benzene successively. The reaction mixture was swirled and heated on a steam bath for two minutes and was then filtered while hot. The filtrate was chromatographed with benzene on neutral alumina grade I. The benzene eluant was evaporated to dryness under reduced pressure, and the red residue was crystallized from ethanol to form bright red crystalline needle of 1,2-diphenyl-naphtho[b]cyclobutadiene (30), m. p. 137-138°.

Anal. Calcd. for C_{24}H_{16} : C, 94.70; H, 5.30.

Found : C, 94.41; H, 5.21.

1,2-Diphenyl-naphtho[b]cyclobutadiene (30) and 2,4,7-Trinitrofluorenone Complex. — A solution of 150 mg. of 1,2-diphenyl-naphtho[b]cyclobutadiene (30) in 10 ml. of benzene and a solution of 155 mg. of 2,4,7-trinitrofluorenone in 7 ml. of benzene were mixed thoroughly. It formed a black solution immediately upon mixing. The mixture was then diluted with 35 ml. of methanol. Black crystalline complex, 260 mg., which formed in a few minutes, was recrystallized from benzene, m. p. 183°.

Anal. Calcd. for C_{37}H_{21}N_{3}O_{7} : C, 71.72; H, 3.41; N, 6.78.

Found : C, 71.50; H, 3.58; N, 6.92.

1,2-Diphenyl-naphtho[b]cyclobutadiene (30) was recovered quantitatively by chromatographing the benzene solution of the black complex through neutral alumina grade I.
1,2-Dibromo-1,2-diphenyl-11naphtho[b]cyclobutene (65). — To a solution of 50 mg. of 1,2-diphenyl-11naphtho[b]cyclobutadiene (30) in 5 ml. of carbon tetrachloride was added drop-wise a 25% solution of bromine in carbon tetrachloride, until the solution became colorless. The solution was then evaporated to dryness in a rotary evaporator under reduced pressure. The residue was then recrystallized from methylene chloride-benzene mixture to give 40 mg. of 1,2-dibromo-1,2-diphenyl-11naphtho[b]cyclobutene (65) which was identical with an authentic sample, m. p. 182-183°.

Oxidation of 1,2-Diphenyl-11naphtho[b]cyclobutadiene (30) to 2,3-Dibenzoylnaphthalene (47). — (a) A red solution of 3 g. of 1,2-diphenyl-11naphtho[b]cyclobutadiene (30) in 2 ml. of benzene was placed near a Hanovia medium pressure ultraviolet lamp under atmosphere. The solution, which was not protected from air, turned colorless in about 30 minutes. The colorless solution was evaporated to dryness and the residue was chromatographed with ether on neutral alumina grade I. The eluant, upon evaporation to dryness, gave 10 mg. of 2,3-dibenzoylnaphthalene (47), m. p. 146°.

(b) A solution of 20 mg. of 1,2-diphenyl-11naphtho[b]cyclobutadiene (30) in 2 ml. of acetone was treated with 15 drops of saturated potassium permanganate in acetone. The mixture, after being acidified with two drops of dilute hydrochloric acid, was heated on a steam bath for 10 minutes. The reaction mixture was then filtered and the filtrate evaporated
to dryness. Recrystallization of the residue from ether gave 16 mg. of 2,3-dibenzoylnaphthalene (47), m. p. 146°.

**Hydrogenation of 1,2-Diphenylnaphtho[b]cyclobutadiene (30) to cis-1,2-Diphenylnaphtho[b]cyclobutene (49a).** — A solution of 150 mg. of 1,2-diphenylnaphtho[b]cyclobutadiene (30) in 10 ml. of benzene and 5 ml. of ethanol was hydrogenated in the presence of palladium-on-charcoal under atmospheric pressure. Upon evaporation of the filtrate from the reaction mixture, 100 mg. of colorless product, m. p. 141.5°, was obtained. The product was identical with cis-1,2-diphenylnaphtho[b]cyclobutene (49a), which was obtained from the catalytic reduction of 1,2-dichloro-1,2-diphenylnaphtho-[b]cyclobutene (29).

5,5a,11b,12-Tetrahydro-5,5a,11b,12-tetraphenyl-5,12-epoxydibenzo[b,h]biphenylene (66); Adduct of 1,2-Diphenylnaphtho[b]cyclobutadiene (30) and 1,4-Diphenyl-2,3-benzo furan (14). — (a) 1,2-Diphenylnaphtho[b]cyclobutadiene (30), 150 mg., and an equimolar amount of 1,4-diphenyl-2,3-benzo-furan (14), 135 mg., were dissolved in 10 ml. of benzene. After 5 hours at room temperature, the mixture was heated on a steam bath for 40 minutes. Upon evaporation of benzene, colorless adduct, 240 mg. was obtained. Recrystallization from benzene-ether mixture gave the analytical sample of 5,5a,11b,12-tetrahydro-5,5a,11b,12-tetraphenyl-5,12-epoxydibenzo[b,h]biphenylene (66), m. p. 297° (decomp.).
Found: C, 91.61; H, 5.39.

(b) 1,2-Dichloro-1,2-diphenyl-naphtho[b]cyclobutene (29), 0.75 g., and an equimolar amount of 1,4-diphenyl-2,3-benzo-furan (14), 0.55 g., were dissolved in 30 ml. of benzene. The mixture was then stirred with an excess of lithium amalgam for 25 hours under nitrogen. After removal of mercury and excess of amalgam by decantation, the solution was treated with 2 g. of activated charcoal and filtered. From the filtrate, 0.45 g. of colorless crystalline adduct (66), m. p. 279° (decomp.) was obtained, which was identical with the material obtained from method (a).

Preparation of 3,8-Diphenyl-naphtho[b]cyclobutene (21).—A mixture of 35 g. of 1,4-diphenyl-2,3-benzo-furan (14) and 40 g. of 3-sulfolene (67) in 250 ml. of benzene was refluxed on a steam bath for 3 days. Without separating the crystals, the reaction mixture was evaporated to dryness under reduced pressure. The solid material was then washed three times with hot water to remove excess of 3-sulfolene. The adduct, 4,9-diphenyl-4,9-epoxy-1,3,4,9-tetrahydronaphtho[2,3-c]-thiophene 2,2-dioxide (68), 50 g., was obtained.

The adduct (68) was mixed with 150 ml. of 40% hydrobromic acid and 200 ml. of glacial acetic acid. The mixture was then heated on a steam bath of 3 days and poured into 500 ml. of cold water with stirring. The solid precipitate
of 4,9-diphenyl-1,3-dihy德ronaphtho[2,3-c]thiophene 2,2-di-
 oxide (69), 47 g., was filtered and washed twice with water, 
methanol and with ether.

The sulfone (69) was then dissolved in 350 ml. of di-
ethyl o-phthalate and heated to boil gently for 8 hours, 
until the evolution of sulfur dioxide ceased. After 
cooling to room temperature, the mixture was poured slowly 
into 600 ml. of 25% sodium hydroxide. The mixture was 
stirred overnight on a steam bath and cooled. The resulting 
brown solid mass was filtered from the mixture and was dried 
in vacuum. Chromatographic purification of the brown 
material on neutral alumina grade I with benzene gave 25 g. 

1-Bromo-3,8-diphenyl-naphtho[b]cyclobutene (71). — To 
a solution of 3 g. of 3,8-diphenyl-naphtho[b]cyclobutene (21) 
in 300 ml. of carbon tetrachloride was added a lump of 1.8 
g. of N-bromosuccinimide and 0.3 g. of dibenzoyl peroxide. 
The mixture was refluxed for 30 minutes on a steam bath. 
After cooling, the reaction mixture was filtered and the 
filtrate evaporated to dryness. Recrystallization of the 
residue from ether and finally from benzene-ether mixture 
gave 2.1 g. of pure 1-bromo-3,8-diphenyl-naphtho[b]cyclo-
butene (71), m. p. 143-144°.

Found: C, 74.98; H, 4.47; H, 20.62.
The same experiment was performed with powered \(\text{N-bromo-succinimide}\). A mixture of 1-bromo and 1,1-dibromo-3,8-diphenylnaphtho[\(b\)]cyclobutene was obtained. Better separation of the two bromides was achieved by acid hydrolysis of the mixture with aqueous alcoholic solution followed by fractional crystallization of the resulting mixture of 1-bromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (71) and 3,8-diphenylnaphtho[\(b\)]cyclobuten-1-one (74) from benzene and ether.

**trans-1,2-Dibromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (22).**

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3,8-Diphenylnaphtho[\(b\)]cyclobutene (21), 15 g., \(\text{N-bromo-succinimide}\), 1.8 g., and dibenzoyl peroxide, 0.3 g., were mixed in 25 ml. of carbon tetrachloride. The mixture was refluxed on a steam bath for 30 minutes. The reaction mixture was then filtered and the filtrate concentrated to 15 ml. and filtered again. After being evaporated to dryness, the residue was crystallized from ether to give 1 g. of trans-1,2-dibromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (22), m. p. 198.5\(^\circ\). (From the mother liquor, 0.1 g. of 1,1-dibromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (72), m. p. 174-175\(^\circ\), was obtained.)

**Anal. Calcd. for \(\text{C}_{24}\text{H}_{16}\text{Br}_2\):**

- \(\text{C}\), 62.09; \(\text{H}\), 3.48; \(\text{Br}\), 34.43.
- **Found:** \(\text{C}\), 62.08; \(\text{H}\), 3.58; \(\text{Br}\), 34.38.

**1,1-Dibromo-3,8-diphenylnaphtho[\(b\)]cyclobutene (72).**

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3,8-Diphenylnaphtho[\(b\)]cyclobutene (21), 1.5 g., \(\text{N-bromo-succinimide}\), 2.7 g., and dibenzoyl peroxide, 0.5 g., were
mixed in 30 ml. of carbon tetrachloride and refluxed on a steam bath for 30 minutes. The reaction mixture was then filtered and the filtrate concentrated to about 15 ml. and filtered again. After evaporation of the filtrate to dryness, the residue was crystallized from ether to give 0.4 g. of \textit{trans}-1,2-dibromo-3,8-diphenylnaphtho[\textit{b}]cyclobutene (22b). From the mother liquor, upon evaporation of ether, 0.75 g. of another crystalline product was obtained. Recrystallization of the latter from acetone gave 0.7 g. of pure 1,1-dibromo-3,8-diphenylnaphtho[\textit{b}]cyclobutene (72), m. p. 174-175\degree

\textbf{Anal.} Calcd. for C\textsubscript{24}H\textsubscript{16}Br\textsubscript{2}: C, 62.09; H, 3.48; Br, 34.43. Found: C, 61.90; H, 3.47; Br, 34.29.

\textbf{1,1,2,2-Tetrabromo-3,8-diphenylnaphtho[\textit{b}]cyclobutene (31).} -- To a solution of 2 g. of 3,8-diphenylnaphtho[\textit{b}]cyclobutene (21) in 200 ml. of carbon tetrachloride was added 7 g. of recrystallized \textit{N}-bromosuccinimide and 0.3 g. of dibenzoyl peroxide. After the mixture was refluxed for 10 hours, additional 3 g. of \textit{N}-bromosuccinimide and 0.2 g. of benzoyl peroxide were added and refluxed for another 5 hours. The reaction mixture was then filtered to remove succinimide and the excess of \textit{N}-bromosuccinimide. The filtrate was then concentrated to 50 ml. and filtered again. The last filtrate, upon evaporation to dryness, gave an oily residue which was crystallized from 30 ml. of ether.
and then recrystallized from benzene-ether mixture to give 1.3 g. of pure 1,1,2,2-tetrabromo-3,8-diphenylnaphtho[b]-cyclobutene (31), m. p. 222-223°.

**Anal.** Calcd. for C_{24}H_{14}Br_{4}; C, 46.34; H, 2.27; Br, 51.39.

**Found:** C, 46.28; H, 2.46; Br, 51.21.

Hydrolysis of 1-Bromo-3,8-diphenylnaphtho[b]cyclobutene (71) to 1-Hydroxy-3,8-diphenylnaphtho[b]cyclobutene (73). --

A solution of 2 g. of 1-bromo-3,8-diphenylnaphtho[b]cyclobutene (71) in 40 ml. of benzene was added dropwise to a solution of 2 g. of silver trifluoroacetate in 40 ml. of benzene, over a period of about 10 minutes. The mixture, after being stirred for 3 hours in the dark, was treated with 1 g. of activated charcoal and filtered. The filtrate, was concentrated to 10 ml. under reduced pressure, and was chromatographed on neutral alumina grade I with benzene. The eluant was evaporated to dryness and the residue recrystallized from benzene-ether mixture to give 1 g. of 1-hydroxy-3,8-diphenylnaphtho[b]cyclobutene (73), m. p. 201-207°.

**Anal.** Calcd. for C_{24}H_{18}O: C, 89.41; H, 5.63.

**Found:** C, 89.19; H, 5.83.

Hydrolysis of 1,1-Dibromo-3,8-diphenylnaphtho[b]cyclobutene (72) to 3,8-Diphenylnaphtho[b]cyclobuten-1-one (74). --

A solution of 50 mg. of 1,1-diphenylnaphtho[b]cyclobutene (72) in 0.6 ml. of benzene was mixed with 0.5 ml. of water,
0.5 ml. of methanol and a drop of concentrated hydrochloric acid. The resulting mixture, after being heated for 30 minutes on a steam bath, was evaporated to dryness. Recrystallization of the residue from benzene-ether mixture gave 20 mg. of 3,8-diphenylnaphtho[b]cyclobuten-1-one (74), m. p. 205°.

**Anal.** Calcd. for C_{24}H_{16}O: C, 89.97; H, 5.03.

Found: C, 89.65; H, 4.72.

**Oxidation of 1-Hydroxy-3,8-diphenylnaphtho[b]cyclobutene (73) to 3,8-Diphenylnaphtho[b]cyclobuten-1-one (74).** A solution of 1 g. of 1-hydroxy-3,8-diphenylnaphtho[b]cyclobutene (73) in 30 ml. of acetone was titrated with Jones' reagent (5 g. of CrO_{3} in 50 ml. of acetic acid, 50 ml. of acetone and 3 ml. of concentrated sulfuric acid), until no more chromium salt precipitated on the addition of more reagent. Methanol was added dropwise to destroy any excess reagent. The reaction mixture was then evaporated to dryness under reduced pressure. The residue, after being washed twice with 5 ml. portions of dilute hydrochloric acid, was recrystallized from benzene-ether mixture to give 0.8 g. of 3,8-diphenylnaphtho[b]cyclobuten-1-one (75), m. p. 205°.

**Anal.** Calcd. for C_{24}H_{16}O: C, 89.97; H, 5.03.

Found: C, 89.47; H, 5.03.
Hydrolysis of 1,2-Dibromo-3,8-diphenylnaphtho[b]cyclobutene (22) to 1,2-Dihydroxy-3,8-diphenylnaphtho[b]cyclobutene (75). -- To a solution of 120 mg. of 1,2-dibromo-3,8-diphenylnaphtho[b]cyclobutene (22b) in 3 ml. of benzene was added a solution of 240 mg. of silver trifluoroacetate in 3 ml. of benzene. The mixture was stirred for four hours in the dark at room temperature, and filtered. The filtrate was then washed five times with 2 ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the dried solution gave an oily residue which was chromatographed over neutral alumina grade II with large volume of benzene. Upon evaporation of the eluant, a colorless crystalline compound was obtained. Recrystallization of the latter from acetone gave pure sample of 1,2-dihydroxy-3,8-diphenylnaphtho[b]cyclobutene (75), m. p. 200-205°, in 65% yield.

Anal. Calcd. for C_{24}H_{18}O_2: C, 85.12; H, 5.36.

Found: C, 85.27; H, 5.38.

Hydrolysis of 1,1,2,2-Tetrabromo-3,8-diphenylnaphtho[b]cyclobutene (31) to 3,8-Diphenylnaphtho[b]cyclobutene 1,2-dione (76). -- A solution of 2 g. of 1,1,2,2-tetrabromo-3,8-diphenylnaphtho[b]cyclobutene (31) in 20 ml. of benzene was added slowly to a solution of 4 g. of silver trifluoroacetate in 50 ml. of benzene over a period of about 10 minutes. After 3 hours of stirring in the dark at room temperature, the mixture was treated with 1 g. of activated
charcoal and filtered. The filtrate was then washed twice with 20 ml. of water and dried over anhydrous magnesium sulfate. Upon evaporation of the solvent benzene, a yellow product, 1.2 g., was obtained. Recrystallization of the yellow product from benzene-ether mixture gave pure 3,8-diphenylnaphtho[b]cyclobutene 1,2-dione (76), double m. p. 238 and 248°.

Anal. Calcd. for C_{24}H_{14}O_{2} : C, 86.21; H, 4.22.

Found : C, 86.51; H, 4.38.

Reduction of 3,8-Diphenylnaphtho[b]cyclobutene 1,2-dione (76) with Sodium Borohydride to 1,2-Dihydroxy-3,8-diphenylnaphtho[b]cyclobutene (75). — Sodium borohydride was added, in small portions, to a solution of 200 mg. of 3,8-diphenylnaphtho[b]cyclobutene 1,2-dione (76) in 10 ml. of benzene and 10 ml. of ethanol, until the yellow color of the diketone (76) disappeared. The solution was then evaporated to dryness under reduced pressure and the residue was washed 3 times with 1 ml. portions of water. Recrystallization of the residue from benzene, and then from acetone gave 120 mg. of 1,2-dihydroxy-3,8-diphenylnaphtho[b]cyclobutene (75), m. p. 200-205°, which was identical with the product obtained from the hydrolysis of trans-1,2-dibromo-compound (22b).

Anal. Calcd. for C_{24}H_{13}O_{2} : C, 85.12; H, 5.36.

Found : C, 84.63; H, 5.45.
Attempted Synthesis of 3,8-Diphenylnaphtho[b]cyclobutadiene (17). -- (a) A solution of 100 mg. of 1-bromo-3,8-diphenylnaphtho[b]cyclobutene (71) in 3 ml. of benzene was treated with one equivalent of potassium t-butoxide in 3 ml. of t-butyl alcohol. The mixture was heated on a steam bath for about 10 minutes and then evaporated to dryness. The residue was washed three times with water. Recrystallization of the residue did not afforded crystalline product, but some amorphous material.

(b) A hot solution of 100 mg. of trans-1,2-dibromo-3,8-diphenylnaphtho[b]cyclobutene (22b) in 3 ml. of benzene was treated with a gram of activated zinc dust, and immediately cooled in an ice bath, and filtered. After being treated with activated charcoal, the filtrate was concentrated. Only polymeric material was obtained.

Trapping of 3,8-Diphenylnaphtho[b]cyclobutadiene (17) with 1,4-Diphenyl-2,3-benzofuran (14). -- A solution of 93 g. of 1,2-dibromo-3,8-diphenylnaphtho[b]cyclobutene (22b) and 54 mg. of 1,4-diphenyl-2,3-benzofuran (14) in 2 ml. of benzene was treated with about 0.5 g. of activated zinc dust for 2 minutes at room temperature. The reaction mixture was then mixed with 0.5 g. of activated charcoal and filtered. The filtrate was evaporated to dryness and the residue taken up in a small amount of ether. The precipitate was recrystallized from benzene-ether mixture to give

**Attempted Synthesis of 1-Bromo-3,8-diphenylnaphtho[b]-cyclobutadiene (77).** -- (a) A solution of 100 mg. of 1,2-dibromo-3,8-diphenylnaphtho[b]cyclobutene (22b) in 5 ml. of benzene was treated with one mole equivalent of potassium t-butoxide in 5 ml. of t-butyl alcohol. The mixture was heated on a steam bath for 30 minutes. The solvent was then evaporated under reduced pressure and the residue was washed twice with 2 ml. portions of water. Purification of the residue by chromatography on neutral alumina and recrystallization from benzene gave only a small amount of brown high melting material (m. p. = 320°).

(b) 1,1-Dibromo-3,8-diphenylnaphtho[b]cyclobutene (72) was treated as the 1,2-dibromo compound (22b) in method (a). The same result was obtained.

**Trapping of 1-Bromo-3,8-diphenylnaphtho[b]cyclobutadiene (77) with 1,4-Diphenyl-2,3-benzofuran (14).** -- (a) A mixture of 140 mg. of 1,2-dibromo-3,8-diphenylnaphtho[b]-cyclobutene (22b) and 65 mg. of 1,4-diphenyl-2,3-benzofuran (14) were dissolved in 2 ml. of warm benzene and solution of 60 mg. of potassium t-butoxide in 3 ml. of t-butyl alcohol was added to the above mixture with stirring. The
resulting mixture, after being heated on a steam bath for 5 minutes, was then evaporated to dryness under reduced pressure. The solid residue was washed twice with 4 ml. portions of water and recrystallized from benzene-ether mixture to give 110 mg. of colorless adduct, 11b-bromo-5,6,11,12-tetraphenyl-5,5a,11b,12-tetrahydro-5,12-epoxy-dibenzo[b,h]biphenylene (78), m. p. 271.5°.

Anal. Calcd for C₄₄H₂₉BrO: C, 80.96; H, 4.47; Br, 12.22.

Found: C, 80.54; H, 4.45; Br, 12.22.

(b) A mixture of 1,1-dibromo-3,8-diphenynaptho[b]cyclobutene and 1,4-diphenyl-2,3-benzofuran (14) was treated by the same procedure in (a). The same result was obtained.

1,2-Dibromo-3,8-diphenynaptho[b]cyclobutadiene (32).—A solution of 3 g. of 1,1,2,2-tetrabromo-3,8-diphenynaptho[b]cyclobutene (31) in 50 ml. of benzene was heated on a steam bath below its boiling point (about 75°) and poured into a flask containing 12 g. of activated zinc dust in 15 ml. of benzene. The mixture was heated on a steam bath for fifteen seconds with swirling and immediately cooled in an ice bath to about room temperature. The cold reaction mixture was then treated with 2 g. of activated charcoal and filtered. The filtrate was evaporated to dryness under reduced pressure and the brown solid residue was washed with a small amount of dry ether. Recrystallization of the solid
gave 0.9 g. of yellow crystalline 1,2-dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32), m. p. 163-165° (decomp.).

**Anal.** Calcd. for C\textsubscript{24}H\textsubscript{14}Br\textsubscript{2}: C, 62.38; H, 3.04; Br, 34.58.

**Found:** C, 62.49; H, 3.10; Br, 34.72.

**Addition of Bromine to 1,2-Dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32).** — A bromine solution in carbon tetrachloride was added to a solution of 50 mg. of 1,2-dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32) in 1 ml. of carbon tetrachloride, until the orange color of bromine persisted. The mixture was then evaporated to dryness under reduced pressure. Upon recrystallization of the residue, 48 mg. of 1,1,2,2-tetrabromo-3,8-diphenyl-naphtho[b]cyclobutene (31), m. p. 222-223°, was obtained.

**1,2-Dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32) and 1,4-Diphenyl-2,3-benzofuran (14) Adduct; 5a,11b-Dibromo-5,6,11,12-tetraphenyl-5,5a,11b,12-tetrahydro-5,12-epoxydibenzo[b,h]biphenylene (79).** — A mixture of 186 mg. of 1,2-dibromo-3,8-diphenyl-naphtho[b]cyclobutadiene (32) and 104 mg. of 1,4-diphenyl-2,3-benzofuran (14) was dissolved in 2 ml. of benzene and heated on a steam bath for 5 minutes. The solution was then concentrated to 1 ml. and cooled. The colorless product, which crystallized in the flask, was filtered and recrystallized from benzene-ether mixture to give 128 mg. of adduct, m. p. 320°. The mother liquor was evaporated to dryness and the gummy residue was taken up in
a small amount of ether. More adduct, 116 mg, was obtained.

**Anal. Calcd. for C_{14}H_{28}Br_{2}O:** C, 72.14; H, 3.85; Br, 21.82.

**Found:** C, 72.59; H, 4.53; Br, 21.30.

**Recrystallization of 1,2-Dibromo-3,8-diphenyl[8]cyclobutadiene (32) with Sodium Methoxide.** — A solution of 150 mg. of 1,2-dibromo-3,8-diphenyl[8]cyclobutadiene (32) in 5 ml. of benzene was mixed with three equivalents of freshly prepared sodium methoxide in 3 ml. of methanol. The mixture was refluxed under nitrogen atmosphere for 2 hours. The solvent was then evaporated to dryness under reduced pressure and the residue was washed three times with 2 ml. portions of water. Recrystallization of the residue from benzene-ether mixture gave 80 mg. of yellow crystalline, 2-bromo-3,8-diphenyl[8]cyclobuten-1-one (80), m. p. 190-191°.

**Anal. Calcd. for C_{24}H_{15}BrO:** C, 72.19; H, 3.80; Br, 20.01.

**Found:** C, 72.10; H, 4.18; Br, 20.14.

**2-Bromo-3,8-diphenyl[8]cyclobuten-1-one (80).** — A solution of 100 mg. of 3,8-diphenyl[8]cyclobuten-1-one (74) in 5 ml. of carbon tetrachloride was refluxed for 1 hour with 56 mg. of N-bromosuccinimide and a catalytic amount of dibenzoyl peroxide. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The oily residue was crystallized from benzene-ether mixture to give
75 mg. of yellow 2-bromo-3,8-diphenylnaphtho[\textit{b}]cyclobuten-1-one (80), m. p. 190-191°, which was identical with the above product.

2-Hydroxy-3,8-diphenylnaphtho[\textit{b}]cyclobuten-1-one (81).—

(a) A solution of 200 mg. of 3,8-diphenylnaphtho[\textit{b}]cyclobutene 1,2-dione (76) in 5 ml. of dioxane was shaken with 1 g. of zinc dust and 0.5 g. of ammonium chloride for 5 hours. The solution was then filtered and evaporated to dryness. The oily residue was washed with 2 ml. of water and recrystallized from benzene to give 100 mg. of pale yellow crystalline 2-hydroxy-3,8-diphenylnaphtho[\textit{b}]cyclobuten-1-one (81), m. p. 226°.


\textit{Found} : \textit{C}, 85.79; \textit{H}, 4.75.

(b) A solution of 80 mg. of 2-bromo-3,8-diphenylnaphtho-[\textit{b}]cyclobuten-1-one (80) in 3 ml. of benzene was added to a solution of one equivalent of silver trifluoroacetate in 2 ml. of benzene. After 2 hours of stirring in the dark, the reaction mixture was treated with 0.5 g. of activated charcoal and filtered. The filtrate was then evaporated to dryness under reduced pressure and the residue was washed twice with 1 ml. portions of water. Recrystallization of the residue from benzene gave 40 mg. of 2-hydroxy-3,8-diphenylnaphtho[\textit{b}]cyclobuten-1-one (81), m. p. 226°.
APPENDIX I ULTRAVIOLET ABSORPTION SPECTRA

The ultraviolet spectra were obtained with a Perkin-Elmer 202 spectrophotometer. Grain alcohol was used as the solvent.
Figure 1
Figure 2

Wave length, m\(\mu\)

Log \(e\)

200 220 240 260 280 300

Chemical structures with different substitutions are shown against the wavelength.
Figure 3

Log ε vs. Wavelength, mμ
Figure 4
Figure 5
Figure 6

Wave length, mµ
Figure 7
Figure 8.
APPENDIX II  NUCLEAR MAGNETIC RESONANCE SPECTRA

The nuclear magnetic resonance spectra were recorded on a Varian A-60 n. m. r. spectrometer using tetramethylsilane as an internal standard. Deuteriochloroform was used as the solvent.
Figure 9
Figure 12
Figure 14
Figure 16
APPENDIX III  INFRARED ABSORPTION SPECTRA

The infrared spectra were determined in pressed potassium bromide disks with Perkin-Elmer, Model 137, Sodium Chloride Spectophotometer.