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PART I
THE SYNTHESIS OF
1,2-DIPHENYLNAPHTO[b]CYCLOBUTADIENE

PART II
THE SYNTHESIS AND REACTIONS OF STABILIZED
2,3-NAPHTHOQUINONOID SYSTEMS

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
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By
James Philip Van Meter, B.Sc.

The Ohio State University
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Approved by

Adviser
Department of Chemistry
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## PART I

### THE SYNTHESIS OF 1,2-DIPHENYLNAPHTO[b]CYCLOBUTADIENE

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PART I

THE SYNTHESIS OF

1,2-DIPHENYLNAPHTO[b]CYCLOBUTADIENE

I. Introduction

The chemistry of cyclobutadiene and its derivatives has long held the interest of organic chemists. With the development of the molecular orbital theory, it became apparent that cyclobutadiene itself does not have aromatic properties, and, at best, can exist only as a transient intermediate.¹

There has been considerable interest in preparing derivatives of cyclobutadiene in order to determine the necessary structural factors which would impart stability to the cyclobutadiene moiety. To date the only stable derivatives of cyclobutadiene are compounds in which both sides of the four-membered ring are fused to aromatic rings, as in biphenylene, and metal complexes such as tetraphenylcyclobutadiene-palladium (II) chloride.² Stable compounds such as phenylcyclobutadiеноquinone³ and benzocyclobutadienoquinone⁴ may be considered to be closely related to cyclobutadiene since all of the four-membered ring carbon atoms are of the sp² type.

The work reported here was directed toward the synthesis of cyclobutadiene derivatives fused to only one aromatic ring. Derivatives of naphthalene substituted in the 2,3-positions seemed to be particularly suited for this purpose. Due to the relative degree of bond fixation in naphthalene, the 2,3-position has less double bond character than does the 1,2-position.\(^5\) With this in mind, it was predicted that the introduction of an additional double bond in the naphtho[b]cyclobutene system would lead to a stable compound which would be intermediate in properties between a dimethylenecyclobutane and a cyclobutadiene system.

The result of incorporating a benzene ring as the stabilizing factor in a cyclobutadiene derivative was shown by Cava and Napier\(^6\) who generated benzocyclobutadiene (1) by treating 1,2-dibromobenzocyclobutene with zinc ethanol.

\[\begin{array}{c}
\text{Cyclobutadiene} \\
\leftrightarrow \\
\text{Cyclobutene}
\end{array}\]

(1)

The cyclobutadiene (1) was too unstable to be isolated and was obtained only as the dimer\(^6\) and in the form of Diels-Alder adducts.\(^7,8\) The mobile electron system of benzene, which imparts considerable

---


cyclobutadienoid character to (1), prevents the compound from being stable.

The comparison of 2,3,6,7-dibenzobiphenylene (2) to the less stable 1,2,7,8-dibenzobiphenylene (3) also points out the destabilizing effect of having a large amount of cyclobutadienoid character in the four-membered ring. Ali and Coulson have discussed the reactivity of (2) and (3) in slightly different terms. They make the statement that "the greater the degree of bond fixation the less the extent of conjugation and the lower the stability." This statement must be modified since the stability of the compounds depends not only on the degree of bond fixation, but more importantly on the direction in which it occurs. If bond fixation forces the compound to have more cyclobutadienoid character as in (3), then it would be expected to be less stable than (2) in which bond fixation favors the non-cyclobutadienoid form.

Cava and Shirley have synthesized naphtho[5]cyclobutene (4) by

\[
\begin{align*}
\text{(5)} & \\
\text{SO}_2 & \\
\Delta & \\
\text{(4)}
\end{align*}
\]

the pyrolysis of 1,3-dihydronaphtho[2,3-\(c\)]thiophene-2,2-dioxide (5).\(^{11}\) The failure to obtain pure mono- or dibromo derivatives of (4) precluded the use of these compounds for the investigation of the then unknown naphtho[\(b\)]cyclobutadiene system.\(^{12}\)

The condensation of monophenyl- (6) and diphenyl-cyclobutadienoquinone with \(o\)-phenylenediamine resulted in the formation of 2-phenylacetylquinoxaline (7)\(^{13}\) and 3-phenylacetyl-2-phenylquinoxaline,\(^{14}\) respectively, rather than the hoped for 3,8-diazanaphtho[\(b\)]-

![Chemical Structure](image)

(6) + (7)

Cyclobutadienes. A similar attempt with dimethylcyclobutadienoquinone\(^{15}\) gave only polymeric product, no quinoxaline derivative was obtained. This is in contrast to the work of Cava and Napier\(^4\) who obtained 1,4-diaza-benzo[\(b\)]biphenylene from benzocyclobutadienoquinone and \(o\)-phenylenediamine.

Nenitzescu and co-workers\(^{16,17}\) generated the first naphtho[\(b\)]-cyclobutadiene by the methods shown in Charts I and II (pages 7,8).


In the first method, adduct (8) (obtained from cyclooctatetraene and dimethyl acetylenedicarboxylate) and 1,4-diphenyl-2,3-benzofuran (9) gave adduct (10). Treatment of adduct (10) with acid gave the aromatized product (11). The thermal decomposition (280°) of (11) gave only polymer. When the decomposition of (11) was carried out in the presence of 1,4-diphenyl-2,3-benzofuran (9), the Diels-Alder adduct (13) of the intermediate 3,8-diphenyl naphtho[b]cyclobutadiene (12) was obtained in 88% yield.

In the second method, the Diels-Alder adduct of (14) of 1,4-diphenyl-2,3-benzofuran and cyclobutene (generated in situ by the reaction of lithium amalgam on 1,2-dibromocyclobutene) was obtained. The treatment of adduct (14) with acid gave 3,8-diphenyl naphtho[b]cyclobutene (15) in an over-all yield of 30-33%. Bromination of (15) with N-bromosuccinimide gave a mixture from which the 1,2-dibromide (16) was isolated in 58% yield. The treatment of the 1,2-dibromide (16) with lithium amalgam generated the unstable 3,8-diphenyl naphtho[b]cyclobutadiene (12) which was trapped with (9) to give the adduct (13) in 14% yield.

In the third approach, Nenitzescu obtained adduct (17) from cis-3,4-dichlorocyclobutene and 1,4-diphenyl-2,3-benzofuran. The treatment of (17) with acid gave cis-1,2-dichloro-3,8-diphenyl-1,2-dihydronaphtho[b]cyclobutene (18). The reaction of (18) and lithium amalgam gave only polymer. The intermediate 3,8-diphenyl naphtho[b]cyclobutadiene (12) could be trapped with (9) to give the Diels-Alder

---

adduct (13). The Diels-Alder adduct (17) was treated with lithium amalgam to give the cyclobutene (19) in 91% yield. Catalytic reduction of (19) gave the cyclobutane (14) (90% yield) which was then treated with acid to give (15) in 64% yield.
Chart I

Generation of 3,8-Diphenynaphtho[b]cyclobutadiene

Method I

(8) \[\text{CO}_2\text{CH}_3\] + (9) \[\text{CO}_2\text{CH}_3\] \(\rightarrow\) (10) \(-\text{H}_2\text{O}\)

(11) \[\text{CO}_2\text{CH}_3\] \(\triangleleft\) [ (12) \(\rightarrow\) (9) \(\rightarrow\) (13) ]

Method II

(9) + (14) \(\rightarrow\) (15) \(\rightarrow\) NBS

(9) \[\text{Br}\] \[\text{Br}\] \(\text{Li(Hg)}\) \[\rightarrow\] [ (12) ] \(\rightarrow\) (13)
Chart II

Generation of 3,4-Diphenynaphtho[b]cylobutadiene

Method III

\[ \text{Li(Hg)} \quad \xrightarrow{\text{Li(Hg)}} \quad \text{[12]} \quad \xrightarrow{\text{9}} \quad \text{[13]} \]

\[ \text{[13]} \quad \xrightarrow{\text{Li(Hg)}} \quad \text{[14]} \quad \xrightarrow{\text{H}_2} \quad \text{[15]} \]
II. Statement of the Problem

The main purpose of this research was the preparation of derivatives of naphthalene substituted in the 2,3-positions which could serve as precursors for the synthesis of 1,2-diphenylnaphtho[b]cyclobutadiene (20).

Two paths were envisaged for this synthesis. The first approach involved the preparation of 1,3-diphenyl-1,3-dihyronaphtho[2,3-c]-thiophene-2,2-dioxide (21). This sulfone could conceivably be converted to 1,2-diphenylnaphtho[b]cyclobutene (22) by analogy with the conversion of 1,3-dihydroisothianaphthene-2,2-dioxide to benzocyclobutene. Further transformations of 1,2-diphenylnaphtho[b]cyclobutene could lead to the corresponding cyclobutadiene (20).

The second approach required the synthesis of 3-benzyl-2-benzoylnaphthalene which could then be monobrominated. Application of an internal Wittig reaction\(^{19,20}\) to the resulting monobromoketone (23) could lead directly to (20).


\(^{19}\) A successful application of an intramolecular Wittig reaction was reported by Bieber and Eisman who obtained 1-phenylcyclopentene by treating triphenyl (4-benzoyl-1-butyl) phosphonium bromide (prepared from triphenylphosphine and 4-benzoyl-1-bromobutane) with sodium ethoxide. T. I. Bieber and E. H. Eisman, J. Org. Chem., 27, 678 (1962).

\(^{20}\) In an attempt to prepare 1-phenylcyclopropene from \(\beta\)-bromopropiophenone, Griffin and Witschard obtained only the dimeric product 1,4-diphenyl-1,4-cyclohexadiene in 12\% yield. C. E. Griffin and G. Witschard, J. Org. Chem., 27, 3334 (1962).
III. Discussion and Interpretation of Results

A suitable starting material for the preparation of 1,3-diphenyl-1,3-dihydronaphtho[2,3-c]thiophene-2,2-dioxide (21) would be the unknown 2,3-dibenzoylnaphthalene (24). The diketone (24) could then be reduced to 2,3-dibenzynaphthalene (25) which could be converted to the sulfone (21) as shown in the following sequence:

\[
\begin{align*}
\text{(24)} & \xrightarrow{\text{NBS}} \text{(25)} & \xrightarrow{\text{1) Na}_2\text{S}} & \xrightarrow{\text{2)} -\text{O}} \text{(21)}
\end{align*}
\]

It is known\(^6\) that \(\alpha,\alpha,\alpha',\alpha''\)-tetrabromo-o-xylene (26) when treated with sodium iodide in ethanol is converted to 1,2-dibromobenzocyclobutene (28) via the o-quinodimethane intermediate (27). It is possible to trap intermediate (27) with dienophiles such as N-phenylmaleimide to form an initial Diels-Alder adduct (29) which then loses two moles of hydrogen bromide to give the corresponding naphthalene derivative (30).\(^{21}\) (See page 11)

In a similar manner, application of this Diels-Alder reaction with trans-1,4-diphenyl-2-butene-1,4-dione (31) as the dienophile should give 2,3-dibenzoylnaphthalene (24). This reaction was carried out by refluxing a solution of the tetrabromide (26) and dienophile (31) in acetone with sodium iodide.\(^{22}\) Work-up of the reaction mixture

\(^{22}\)This reaction was first carried out by Dr. M. J. Mitchell of this department.
gave in good yield a crystalline compound, m.p. 253-256°, which shows a strong carbonyl absorption at 6.1 μ in the infrared. The elemental analysis was close enough to C_{24}H_{16}O_{2} that it was assumed to be the diketone (24). However, it soon became apparent that the product of this reaction was not the desired diketone. Attempts to reduce this compound to 2,3-dibenzynaphthalene gave only starting material or products which could not be identified. The reducing conditions used included the Clemmensen procedure, the use of lithium aluminium hydride-aluminium chloride complex, and catalytic reduction with copper chromite at 200° and hydrogen pressure of 1700 lbs./sq. in. No further work was done to determine the true structure of this compound.

\[
\begin{align*}
&\begin{array}{c}
\text{CHBr}_2 \\
\text{CHBr}_2
\end{array} \rightarrow \begin{array}{c}
\text{NaI} \\
\text{CHBr}
\end{array} & \begin{array}{c}
\text{CHBr} \\
\text{CHBr}
\end{array} & \begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} \\
&\begin{array}{c}
\phi-\text{C}=\text{C}-\phi \\
\text{H}
\end{array} & \begin{array}{c}
\phi-\text{N} \rightleftharpoons \text{O} \\
\text{O}
\end{array} & \begin{array}{c}
\phi-\text{N} \rightleftharpoons \text{O} \\
\text{O}
\end{array} \\
&\begin{array}{c}
\text{Br} \\
\text{C}=\phi
\end{array} & \begin{array}{c}
\text{H} \\
\text{H}
\end{array} & \begin{array}{c}
\text{N}-\phi \\
\text{N}
\end{array}
\end{align*}
\]
The synthesis of 2,3-dibenzoylnaphthalene (24) was accomplished starting with the readily available 2,3-dimethylnaphthalene (32). The procedure of Friedman\textsuperscript{23} was used to oxidize 2,3-dimethylnaphthalene to the corresponding diacid (33). Freund and Fleischer\textsuperscript{24} have prepared the anhydride (34) by heating the diacid to 245-250°, by sublimation, and by treating the diacid with thionyl chloride or phosphorous pentachloride. In the present work, the formation of the anhydride was achieved by boiling the diacid in acetic acid-acetic anhydride.

Following the procedures in the literature,\textsuperscript{25,26} the known 3-benzoyl-2-naphthoic acid (35) was prepared by the Friedel-Crafts reaction of the anhydride (34) with benzene.

\begin{center}
\begin{align*}
23\text{L. Friedman, Org. Syn.,} & 43, 60 (1963). \\
24\text{M. Freund and K. Fleischer, Ann.,} & 399, 215 (1913); 402, 68, 70 (1914). \\
25\text{H. Waldmann and H. Mathiowitz, Ber.,} & 64, 1713 (1931). \\
26\text{E. deB. Barnett and R. A. Lowry, Ber.,} & 1649 (1932).
\end{align*}
\end{center}
The ketoacid (35) was reduced to the lactone (36) with sodium borohydride in a manner similar to Newman's preparation of 3-phenylphthalide from o-benzoylbenzoic acid. The reaction mixture was acidified with dilute hydrochloric acid and the product was extracted with methylene chloride. The organic extract was then washed with 1N hydrochloric acid to insure closure of the intermediate hydroxyacid to the lactone. Lactone (36), obtained in 80% yield, shows a strong absorption in the infrared at 5.67 μ (lactone carbonyl).

The addition of excess phenylmagnesium bromide in ethyl ether to a suspension of lactone (36) in tetrahydrofuran gave, after work-up, the lactol (37) in 91% yield. The reaction mixture was decomposed under weakly acidic conditions by using aqueous ammonium chloride solution in order to prevent decomposition of the lactol (37) (See Part II of this dissertation). The elemental analysis and the infrared spectrum which shows a strong hydroxy absorption at 3.0 μ and the absence of a carbonyl absorption confirmed the structure of (37).

The oxidation of lactol (37) with chromic oxide-pyridine reagent gave the authentic 2,3-dibenzoylnaphthalene (24), m.p. 143-145°, in 87% yield.

At this point it was possible to modify the proposed reaction sequence for the preparation of sulfone (21). (See page 10) It was discovered by R. H. Schlessinger that certain 1,4-diols such as 7,12-dihydropleiadene-7,12-diol (38) could be converted to the

corresponding sulfide (39) by the treatment with phosphorus pentasulfide. In addition, Schlessinger discovered that the irradiation of the related sulfone (40) liberated sulfur dioxide with the formation of pleiadene dimer (41). The irradiation of sulfone (21) was therefore considered.

The diketone (24) was reduced with lithium aluminum hydride in ethyl ether to the diol (42) in 96% yield. The treatment of diol (42) with phosphorus pentasulfide in carbon disulfide gave the cyclic sulfide (43). The sulfide was not characterized but was oxidized with peracetic acid to the sulfone (21) in 39.6% yield based on diol (42).

Irradiation of sulfone (21) in benzene solution with a Hanovia medium pressure lamp with a quartz probe gave trans-1,2-diphenyl-naphtho[b]cyclobutene (44) in 39% yield. B. Hwang\(^2\) has prepared the corresponding cis-derivative (46) by the catalytic reduction of 1,2-dichloro-1,2-diphenyl-naphtho[b]cyclobutene (45). The stereochemistry of (44) and (46) was based on the positions of the benzylic protons in the nuclear magnetic resonance spectrum. The benzylic protons of the trans isomer (44) are more shielded (\(\tau=5.33\) p.p.m.) than those

of the cis isomer (46) (γ = 4.66 p.p.m.). The same relationship was observed by Carpino\(^{30}\) for the cis and trans 1,2-diphenylbenzocyclobutenes. In this case the benzylic protons appear at γ = 5.56 p.p.m. and γ = 4.08 p.p.m. for the trans and cis isomers respectively.

Integration of the nuclear magnetic resonance spectrum for the trans isomer (44) accounted for 16 aromatic protons between γ = 1.08 p.p.m. and γ = 2.77 p.p.m. and the two benzylic protons.

Refluxing a solution of trans-1,2-diphenynaphtho[\(b\)]cyclobutene (44) in N,N-dimethylformamide caused rearrangement to 5-phenyl-5,12-dihydronaphthacene (47). The rearrangement is assumed to occur by way of the intermediate quinodimethane (44a) which then undergoes further thermal isomerization to the intermediate (44b). Intermediate (44b) has not only less orbital overlap stabilization but also a more favorable conformation for the ring closure to form (47).

The nuclear magnetic resonance spectrum of (47) integrates for two protons at $\tau=6.06$ p.p.m. which is attributed to the two methylene protons. This is in close agreement to the methylene protons of 9,10-dihydroanthracene which occur at $\tau=6.13$ p.p.m.\(^{31}\) The single methine proton, which is deshielded by the phenyl group, appears at lower field ($\tau=4.68$ p.p.m.).

The analogous rearrangement of 1,2-diphenylbenzocyclobutene to 9-phenyl-9,10-dihydroanthracene has been assumed to occur although the experimental conditions for the reaction, as such, do not appear in the literature. In a paper discussing the reactivity of 1,2-diphenylbenzocyclobutene, Jensen\(^{32}\) states that this compound "is obtained essentially unchanged from hot alcohol and other solvents." By refluxing a solution of cis-1,2-diphenylbenzocyclobutene in carbon tetrachloride for 14 hours, Carpino\(^{30}\) obtained the corresponding trans isomer in 50% yield. No mention of 9-phenyl-9,10-dihydroanthracene was made. In an attempt to prepare 1,2-diphenylbenzocyclobutene by the pyrolysis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (48), Cava\(^{33}\) obtained 9-phenyl-9,10-dihydroanthracene as the only


product. A similar result was observed by Jensen and Coleman. \(^{32}\)

It is apparent that the conditions needed for the thermal expulsion of sulfur dioxide from sulfone (48) are too severe for the formation of 1,2-diphenylbenzocyclobutene.

Refluxing a solution of sulfone (21) in \(\text{N,N-dimethylformamide}\) under the same conditions used to effect rearrangement of (44) to (47) resulted in the recovery of starting sulfone. From this experiment it can be concluded that the conditions needed for the thermal expulsion of sulfur dioxide from sulfone (21) must be more drastic than those needed to effect the rearrangement to (47). Hence, the synthesis of 1,2-diphenylnaphtho\([b]\)cyclobutene (44) from sulfone (21) under pyrolytic conditions would not appear to be a feasible reaction.

Heating a mixture of \(\text{trans}\)-1,2-diphenylnaphtho\([b]\)cyclobutene (44) and \(\text{N-phenylmaleimide}\) without solvent at 170±5°C gave a 77% yield of the Diels-Alder adduct (49). The reaction of 1,2-diphenylbenzocyclobutene (50) occurs under much milder conditions.\(^{32}\) The reaction of a molar amount of maleic anhydride with (50) in carbon tetrachloride at room temperature for 48 hours gave a nearly quantitative yield of the expected adduct. In comparison, a solution of the naphtho\([b]\)-cyclobutene (44) and an excess of maleic anhydride in carbon tetrachloride for 48 hours at room temperature resulted in the recovery of 97% of the starting cyclobutene (44). Since the intermediate in this reaction is the quinodimethane, it would be expected that (50) would react easier than (44) since less energy is required to disrupt the benzene system than both aromatic rings of the naphthalene system.
Before describing additional reaction of trans-1,2-diphenyl-
naphtho[b]cyclobutene (44), the second approach to 1,2-diphenylnaphtho-
[b]cyclobutadene (20) will be considered.

Although the monobromoketone (23) which was required for the
internal Wittig reaction could not be prepared, it was possible to
utilize its precursor, 3-benzyl-2-benzoylnaphthalene (55), in a second
method of preparing trans-1,2-diphenylnaphtho[b]cyclobutene (44). This
sequence of reactions is outlined in Chart III.

The reduction of 3-benzoyl-2-naphthoic acid (35) to the 3-benzyl
derivative (51) was carried out by deB. Barnett and Lowry using zinc,
ammonia, copper sulfate, and sodium sulfate solution. Efforts to repeat
this procedure gave poor results. The catalytic reduction of the keto-
acid (35) gave the 3-benzyl derivative (51) in 58% yield. The reaction
of 3-benzyl-2-naphthoic acid (51) with thionyl chloride gave the acid
chloride (52) which was not isolated but treated with ammonia gas to
give 3-benzyl-2-naphthamide (53) in 93% yield. Dehydration of amide
(53) with phosphorus oxychloride gave 3-benzyl-2-cyanonaphthalene (54)
in 77% yield. A solution of nitrile (54) in benzene was added to a
refluxing solution of phenylmagnesium bromide in ethyl ether. Work-up
of the reaction mixture with hydrochloric acid gave the solid imine
hydrochloride. The hydrolysis of the imine hydrochloride was accomp-
lished by heating with ethanol-dilute hydrochloric acid for 4 days on
Chart III

Synthesis of trans-1,2-Diphenynaphtho[b] cyclobutene

1. BOH
2. H^+ CH_2OH

(35) → (51) → (52) → (53) → (54) → (55) 

(53) \[\text{NH}_3\] → (54) \[\text{POCl}_3\] → (55) \[\text{MgBr}\] → (23) \[\text{Br}_2/hv\] → (24) \[\text{LiAlH}_4/\text{AlCl}_3\] 

(25) \[\text{Br}/hv\] → (23) \[\text{Br}_2/hv\] → (24) 

(25) \[\text{Br}/hv\] → (23) \[\text{Br}_2/hv\] → (24) 

1. NaBH_4 
2. H^+ 

(55) → (56) → (57) → B^\ominus
the steam bath. The 3-benzyl-2-benzoylnaphthalene (55) was obtained in 69% yield. The reduction of ketone (55) with lithium aluminum hydride-aluminum chloride complex gave the expected 2,3-dibenzyl-naphthalene (25) in 81% yield.

The addition of a molar equivalent of bromine to an irradiated solution of ketone (55) in carbon tetrachloride gave 2,3-dibenzoylnaphthalene (24) in 75% yield (based on bromine). The unreacted monoketone (52) was not isolated. No further work was done to elucidate the mechanism of the formation of the diketone (24). Since the monobromoketone (23) could not be prepared under these relatively mild conditions, the application of an internal Wittig reaction to the possible synthesis of 1,2-diphenylnaphtho[b]cyclobutadiene (20) was discontinued.

The monoketone (55) proved to be a valuable intermediate since it could be converted into trans-1,2-diphenylnaphtho[b]cyclobutene (44). The monoketone (55) was reduced with sodium borohydride in ethanol to the corresponding alcohol (56). The alcohol was obtained as an oil which solidified on standing and was of sufficient purity to be used for the subsequent reactions. Recrystallization of a sample from one experiment gave the analytical sample, m.p. 113-114°. The reaction of alcohol (56) with excess thionyl chloride at 0° gave the chloride (57) obtained as an oil which was not characterized. Treatment of the chloride (57) with excess potassium t-butoxide in t-butyl alcohol gave trans-1,2-diphenylnaphtho[b]cyclobutene (44) in 80% yield based on the starting ketone (55). The cyclobutene (44) obtained from the ketone was identical to that obtained by the photolysis of sulfone (21).
A reasonable mechanism for the formation of (44) from the chloride (57) is shown in Chart IV. The base abstracts a proton from (57) to give the intermediate carbanion (58). Elimination of a chloride ion from (58) gives the quinodimethane structure (44a) which then closes to give (44).

Free radical bromination of trans-1,2-diphenynaphtho[b]cyclobutene (44) with N-bromosuccinimide in carbon tetrachloride gave 1,2-dibromo-1,2-diphenynaphtho[b]cyclobutene (59) in 70% yield. (Chart IV) Debromination of (59) with zinc dust in benzene gave 1,2-diphenynaphtho[b]cyclobutadiene (20) isolated as the 2,4,7-trinitrofluorenone complex in 30% yield. The complex was decomposed on alumina to give pure (20) obtained as bright red needles. Treatment of dibromide (59) with sodium iodide in acetone gave a 16% yield of (20).

The cyclobutadiene (20) is identical to the material first obtained by Hwang from the dechlorination of 1,2-dichloro-1,2-diphenynaphtho[b]cyclobutene (45) with zinc dust. The dichloronaphtho[b]-butene (45) was prepared from 1,2-dimethoxy-1,2-diphenynaphtho[b]-cyclobutene. The synthesis of the dimethoxy derivative involved the simultaneous formation of the naphthalene system fused to the four-membered ring from a simple bisacetylenic benzene derivative.

Evidence that bonds 2a-3 and 8a-9a in (20) are fixed to a remarkable degree as in (20a) comes from the nuclear magnetic resonance spectrum of (20). In addition to the 14 protons in the usual aromatic region, two protons appear as a sharp peak at \( \tau = 3.50 \) p.p.m. which are considered

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Chart IV
Preparation of 1,2-Diphenynaphtho [b] cyclobutadiene

(57) $\xrightarrow{\text{B}^-} (58)$

(44) $\xrightarrow{\text{NBS}} (59)$

(59) $\xrightarrow{\text{Zn}} (20a)$

(20a) $\xrightarrow{\text{Zn}} (20b)$
to be those at C-3 and C-8. The olefinic protons of cis-stilbene appear at $\tau=3.45$ p.p.m. and thus substantiate this assignment. No olefinic protons appear at higher field than the phenyl protons at $\tau=2.77$ p.p.m. and $\tau=3.06$ p.p.m. for the trans and cis-1,2-diphenyl-naphtho[b]cyclobutene, respectively.

It is concluded from the nuclear magnetic resonance data that the cyclobutadiene (20) is best represented as a dimethylene cyclobutene derivative as in (20a) and that the cyclobutadienoid character of the four-membered ring is very small.

The addition of one equivalent of bromine to (20) in carbon tetrachloride solution at 0° resulted in the instantaneous formation of the dibromide (59) which is identical (m.p. and infrared spectrum) to the dibromide obtained from the cyclobutene (44) and N-bromosuccinimide (NBS). Since there appears to be no known case of preferential ionic cis addition of bromine to an olefin, it is concluded that the dibromide obtained by the bromine addition to (20) has the trans configuration as shown in Chart IV. The stereochemistry of the dibromide (59) from the NBS reaction is thus assumed to be trans.

It is of interest to discuss the possible mechanism of the formation of the trans dibromide (59) from the NBS reaction. It is known that the active brominating agent in free radical NBS reactions is

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molecular bromine which is formed in low concentration by the fast ionic reaction of hydrogen bromide with NBS. The molecular bromine thus formed is the source of bromine atoms which abstract hydrogen atoms from the substrate to give the benzylic or alkyl radical. These radicals then react with molecular bromine to give the product plus the chain carrying bromine atoms (See Chart V).

The intermediate monobromide (60) is considered to be formed in this manner. Hydrogen abstraction from (60) could give the intermediate (61) represented as a bridged radical in which the bromine atom oscillates between the two carbon atoms. The results of electron paramagnetic resonance studies of the light catalyzed addition of hydrogen bromide to olefins has been explained in terms of this oscillating bromine atom type structure. The bridged radical is also consistent with the facile 1,2-migrations of bromine observed by Skell. Further evidence for the bridged radical was obtained from the photobromination of optically active 1,2-dibromo-2-methylbutane. In this case the bridged radical is capable of maintaining the stereochemical configuration until the reaction with bromine occurs. W. Thaler has obtained trans-1,2-dibromocyclohexane as the major product in the photobromination of bromocyclohexane with bromine. He suggested that the intermediate bromoalkyl radical may exist as

Chart IV

Trans-1,2-Dibromo-1,2-Diphenynaphtho [b] cyclobutene

\[ \text{NBS} + \text{HBr} \rightarrow \text{Br}_2 + \text{succinimide} \]

\[ \text{Br}^+ + \text{R} \rightarrow \text{HBr} + \text{R}^+ \]

\[ \text{R}^+ + \text{Br}_2 \rightarrow \text{RBr} + \text{Br}^+ \]

Path B

\[ -\text{Br}^+ \]

Path A

\[ \text{Br}_2 \]

(20) \[ \text{Br}_2 \rightarrow \]

(59)

(60)

(61)
three-membered ring species which then reacts with molecular bromine to give the trans-1,2-dibromocyclohexane.

In a similar fashion, attack of molecular bromine on the bridged radical (61) would give trans-1,2-dibromo-1,2-diphenyl[2,3-c]cyclobutene (59) (Chart V, Path A). The bromine atom in the intermediate (61) is very mobile and it is conceivable that it could lose a bromine atom to give the cyclobutadiene (20) which could then add bromine in a trans ionic fashion to give the trans dibromide (59) (Chart V, Path B).

During the course of this work, it was discovered that 3-sulfolene (62) (2,5-dihydrothiophene-1,1-dioxide) undergoes the Diels-Alder reaction with active dienes. There appears to be no report of a Diels-Alder reaction with 3-sulfolene in the literature. The Diels-Alder reaction of 2-sulfolene with butadiene, 2,3-dimethylbutadiene, and cyclopentadiene to give the corresponding adducts has been reported by Alder.42

An alternative synthesis to the known 3,8-diphenyl[2,3-c]cyclobutene (15) was now possible. Refluxing a mixture of 1,4-diphenyl-2,3-benzofuran (9) and excess 3-sulfolene in benzene for 64 hours gave a 97% yield of adduct (63). The work-up of this reaction is relatively simple due to the solubility of 3-sulfolene in water. Treatment of the adduct (63) with hydrobromic acid in acetic acid gave the aromatized product, 4,9-diphenyl-1,3-dihydrophtpho[2,3-c]thiophene-2,2-dioxide (64) in 94% yield. The pyrolysis of sulfone (64) in refluxing diethyl phthalate for 5 hours and 20 minutes resulted in the

recovery of 26% of the starting sulfone (64) and a 77% yield of 3,8-
Although the melting point of the cyclobutene (15) prepared in this
manner was 6 degrees higher than reported,\textsuperscript{16,17} the infrared red and
ultraviolet spectrum of (15) are in agreement with the literature values.
This procedure for the synthesis of the cyclobutene (15) from readily
available starting materials is superior to that of \textsuperscript{16}Nenitzescu and
Avram.\textsuperscript{17}

\[
\begin{align*}
\text{(62)} & \quad + \quad \text{(9)} \quad \rightarrow \quad \text{(63)} \quad \rightarrow \quad \text{(64)} \\
\text{(64)} & \quad \Delta \quad \rightarrow \quad \text{(15)} \quad \quad \text{(21)}
\end{align*}
\]

The attempted photolysis of sulfone (64) for 17 hours at 8\textdegree
with a Hanovia medium pressure lamp with a quartz probe resulted in
the recovery of starting sulfone.

It can be seen by comparing the reactivity of sulfone (21) and
sulfone (64) under photolytic and pyrolytic conditions that by
judicious choice of the reaction conditions the sulfone approach to
cyclobutenes fused to aromatic rings has considerable synthetic utility.
IV. Experimental

All melting points are uncorrected. Microanalyses were determined by Midwest Microlab Inc., Indianapolis, Indiana, Schwartzkopf Laboratories, Woodside, New York, and Alfred Bernhardt, Max-Planck Institute, Mulheim (Ruhr), Germany.

The Reaction of a,α,α',α'-Tetrabromo-o-xylene (26) with trans-1,4-Diphenyl-2-butene-1,4-dione (31)—To a mixture of sodium iodide (255 g.) and trans-1,4-diphenyl-2-butene-1,4-dione (75 g.) in reagent grade acetone (1 l.) contained in a three neck flask equipped with a stirring motor and a reflux condenser, was added tetrabromide (26) (105 g.). The mixture was refluxed with stirring for three days. The reaction mixture was cooled to room temperature and the product was removed by filtration. After washing with acetone, the product was suspended in water to remove the inorganic material. The product was again filtered and air dried to give 70 g. of material. Recrystallization from acetonitrile gave m.p. 253-256°, as white needles.

Anal. Calcd. for C_{24}H_{16}O_4: C, 85.69; H, 4.79.
Found: C, 84.78; H, 5.13.

Naphthalene-2,3-dicarboxylic Anhydride (34)—The oxidation of 2,3-dimethylnaphthalene to the corresponding diacid (33) was carried out using the procedure of Friedman. This procedure is recorded here for the sake of completeness.

A mixture of 2,3-dimethylnaphthalene (200 g.), sodium dichromate (1000 g.) and water (1.8 l.) in a rocking autoclave (3.25 l. capacity) was heated for 18 hours at 250°. After cooling to room temperature,
the autoclave was opened and washed with warm water to remove all products. The combined washings were filtered with suction and the chromic oxide was washed with water until acidification of an aliquot gave no precipitate of diacid. The clear alkaline filtrates and wash liquors were combined and extracted with ethyl ether to remove any starting material. The aqueous solution was acidified with 1.1 hydrochloric acid and the product was removed by filtration to give 227 g. (82%) of naphthalene-2,3-dicarboxylic acid. The diacid (33) was heated to boiling in acetic anhydride (600 ml.) and acetic acid (310). After standing overnight, the product was removed by filtration to give 157 g. (79%) of naphthalene-2,3-dicarboxylic anhydride obtained as plates, m.p. 250-251° (lit.24 m.p. 246°).

3-Benzoyl-2-naphthoic Acid (35).—The procedures of Waldmann25 and deB. Barnett26 were followed in this synthesis. To a mixture of anhydride (34) (26 g.) in benzene (250 ml.) was added aluminum chloride (36 g.). The mixture was heated on the steam bath for 15 hours with occasional swirling during the first 20 minutes. The reaction mixture was carefully hydrolyzed with 1.1 hydrochloric acid. Chloroform and concentrated hydrochloric acid were added until all the solid material went into solution. The organic layer was separated and the aqueous layer was extracted once with chloroform. The combined organic extract was washed once with water and then four times with aqueous sodium carbonate solution. The basic extract was acidified with concentrated hydrochloric acid and the product was removed by filtration and washed with water. After drying, the product
was crystallized from chloroform-Skelly B to give 30.7 g. (89%) of 3-benzoyl-2-naphthoic acid, m.p. 212-214° (lit.25 m.p. 209.5°).

**Lactone (36).** The preparation of the lactone (36) was accomplished by using Newman's procedure for the preparation of 3-phenylphthalide. To a solution of ketoacid (35) (37.7 g.) in water (750 ml.) and enough sodium hydroxide for solution was added sodium borohydride (25 g.). After stirring for 70 hours at room temperature, the reaction mixture was made almost neutral by the careful addition of dilute hydrochloric acid. An additional 5 g. of sodium borohydride was then added in small portions to the reaction mixture. After stirring for a final 46 hours, the mixture was acidified by the slow addition of dilute hydrochloric acid. The product was then extracted with methylene chloride. The organic extract was shaken with 1:1 hydrochloric acid and then washed once with water and finally three times with dilute aqueous sodium bicarbonate solution. The organic solution was dried over sodium sulfate and filtered. The filtrate was evaporated to dryness in vacuo and the residue recrystallized from benzene to give 29.0 g. (80%) of the lactone (36), m.p. 153-155°.

**Anal.** Calcd. for C_{18}H_{12}O_{2} (260.28): C, 83.06; H, 4.65.

Found: C, 83.59; H, 5.03.

**Lactol (37).** A solution of phenylmagnesium bromide (0.12 mole) in anhydrous ethyl ether (90 ml.) was added over a period of 20 minutes to a magnetically stirred suspension of lactone (36) (15.6 g., 0.06 mole) in anhydrous tetrahydrofuran (200 ml.) cooled to 0°. After stirring for an additional 10 minutes, the reaction mixture was
poured into a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted twice with ethyl ether. The combined organic extracts were dried with anhydrous sodium sulfate. The solution was filtered and the filtrate was concentrated in vacuo to a volume of 30-40 ml. The solid product was removed by filtration and washed with Skelly F to give 18.5 g. (91%) of lactol (37), m.p. 149-157° dec.

**Anal.** Calcd. for C_{24}H_{18}O_{2} (338.38): C, 85.18; H, 5.36.

Found: C, 85.02; H, 5.50.

**2,3-Dibenzoylnaphthalene (24).**—To pyridine (150 ml.), cooled to 0°, was added in small portions and with stirring chromic oxide (9.5 g.). To the resulting slurry was added lactol (37) (9.01 g.). The mixture was stirred at room temperature for 4.5 days. The reaction mixture was then poured into water and extracted with 1:1 ethyl ether-benzene. The organic extract was washed with water and dilute hydrochloric acid. The extract was dried over magnesium sulfate, filtered, and the filtrate evaporated to dryness in vacuo. The resulting oil was crystallized from ethyl ether to give 7.82 g. (87%) of 2,3-dibenzoylnaphthalene (24), m.p. 143-145°.

**Anal.** Calcd. for C_{24}H_{16}O_{2} (336.37): C, 85.69; H, 4.79.

Found: C, 85.82; H, 4.69.

**Diol (42).**—Diketone (24) (22.66 g.) was added to a refluxing solution of excess lithium aluminum hydride in ethyl ether by means of a Soxhlet extractor. Approximately two days were required for the introduction of the diketone. The excess lithium aluminum hydride was then decomposed with methanol followed by aqueous ammonium chloride
solution. The resulting suspension was extracted four times with ethyl ether. The ether extract was concentrated to a smaller volume, dried over sodium sulfate and filtered. The product crystallized upon the addition of Skelly F to give 21.90 g. (96%) of diol (42), m.p. 136-164°. Chromatography with benzene on acid washed alumina grade III followed by crystallization from benzene-Skelly B gave the analytical sample, m.p. 163-165°.

Anal. Calcd. for C_{24}H_{20}O_2 (340.40): C, 84.68; H, 5.92.

Found: C, 84.67; H, 5.95.

1,3-Diphenyl-1,3-dihyronaphtho[2,3-a]thiophene-2,2-dioxide (21).

To a mixture of phosphorus pentasulfide (11.2 g.) in carbon disulfide (150 ml.) was added diol (42) (7.076 g.). This mixture was stirred at room temperature for 4 days. The reaction mixture was filtered and the filtrate was evaporated to dryness in vacuo. The residue was washed with benzene. The benzene washings were evaporated to dryness in vacuo and the residue was taken up in glacial acetic acid. Excess peracetic acid was then added and the solution was stirred at room temperature for 2 days. The reaction mixture was poured into aqueous sodium chloride solution. The product was extracted with methylene chloride. This extract was washed with water and dilute aqueous sodium bicarbonate solution, dried over sodium sulfate and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from benzene to give 3.063 g. (39.6%) of sulfone (21), m.p. 252-256° dec. Chromatography with benzene on neutral alumina grade IV followed by crystallization from benzene-cyclohexane gave the analytical sample, m.p. 248-251° dec., obtained as fine needles.
trans-1,2-Diphenynaphtho[b]cyclobutene (44) from Sulfone (21).—A solution of sulfone (21) (0.384 g.) in dry reagent grade benzene (170 ml.) was irradiated with a Hanovia medium pressure lamp model #6798 (quartz probe) for 4 hours and 20 minutes. The reaction mixture was then evaporated to dryness in vacuo and the residue was chromatographed with benzene on neutral alumina grade III. The eluant was evaporated to dryness in vacuo and the residue was chromatographed again with hexane on neutral alumina grade III. The eluant was evaporated to dryness in vacuo and the residue was crystallized from hexane to give 0.125 g. (39.4%) of trans-1,2-diphenynaphtho[b]cyclobutene, m.p. 155-157°. Recrystallization from petroleum ether, b.p. 30-60°, gave the analytical sample, m.p. 157-158°, obtained as plates.

5-Phenyl-5,12-dihydronaphthacene (47).—A solution of trans-1,2-diphenynaphtho[b]cyclobutene (44) (0.422 g.) in N,N-dimethylformamide (20 ml.) was refluxed for 3.75 hours. After cooling, the reaction mixture was poured into aqueous sodium chloride solution and the product was extracted with benzene. The organic extract was washed with water, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was recrystallized from carbon tetrachloride-Skelly B to give 0.349 g. (83%) of 5-phenyl-5,12-dihydronaphthacene, m.p. 149-150°. Recrystallization from the same solvent system gave the analytical sample, m.p. 149-150°.

Found: C, 93.77; H, 6.16.

**Sulfone (21) in N,N-Dimethylformamide**—A solution of sulfone (21) (0.060 g.) in N,N-dimethylformamide (20 ml.) was refluxed for 3 hours and 20 minutes. After cooling to room temperature, the reaction mixture was poured into aqueous sodium chloride solution. The product was removed by filtration and air dried. Chromatography with benzene on neutral alumina grade IV gave 0.060 g. (100%) of starting sulfone (21), m.p. 253-254° dec., recrystallized from methylene chloride-hexane. The infrared spectrum of this material was identical to that of the starting sulfone (21).

**N-Phenylmaleimide Adduct (49)—**A finely ground mixture of trans-1,2-phenylmaleimide (0.378 g.) in a pyrex test tube was heated at 170±5° in a salt bath for 12 minutes. After cooling the solid material was dissolved in methylene chloride and chromatographed with methylene chloride on neutral alumina grade III. The eluant was evaporated to dryness in vacuo and the residue was crystallized from methylene chloride-hexane to give 0.222 g. (77%) of adduct (49), m.p. 273-276°. Chromatography with chloroform on acid washed alumina grade III followed by crystallization from benzene-hexane gave the analytical sample, m.p. 278-279°.

**trans-1,2-Diphenyl[naphtho]cyclobutene (44) and Maleic Anhydride**—A solution of trans-1,2-diphenyl[naphtho]cyclobutene (0.063 g.) and maleic anhydride (0.129 g.) in carbon tetrachloride (15 ml.) was
allowed to stand at room temperature for 48 hours. The solution was then chromatographed with carbon tetrachloride on neutral alumina grade I. The eluant was evaporated to dryness in vacuo to give 0.061 g. (97%) of starting naphtho[b]cyclobutene (44), m.p. 157-158°. The infrared spectrum of this sample was identical to that of the starting material.

3-Benzyl-2-naphthoic Acid (51).—To a warm solution of 3-benzoyl-2-naphthoic acid (35) (10 g.) in 1:1 glacial acetic acid-95% ethanol (200 ml.) was added 5% palladium on carbon (3 g.). The mixture was hydrogenated on a Parr shaker for 22.5 hours with an initial hydrogen pressure of 49 lbs./sq. in. The reaction mixture was then warmed on a steam bath to dissolve all the organic material. The hot mixture was filtered through a Celite pad to remove the catalyst. The filtrate was poured into water and the product was removed by filtration, dried and crystallized from chloroform-Skelly F to give 5.56 g. (58.6%) of 3-benzyl-2-naphthoic acid (51), m.p. 199-201° (lit.26 m.p. 204°).

3-Benzyl-2-naphthamide (53).—To a solution of acid (51) (7.496 g.) in 1:1 methylene chloride-benzene (80 ml.) was added pyridine (0.2 ml.) and thionyl chloride (4.8 ml.). After refluxing for 2 hours on the steam bath, methylene chloride (100 ml.) was added. The reaction mixture was then cooled in an ice bath and saturated with ammonia gas. The reaction mixture was then poured into methylene chloride and water. The organic layer was separated and the aqueous layer was extracted once with methylene chloride. The combined organic extract was washed twice with dilute aqueous sodium carbonate solution and once with water. The organic extract was dried over sodium sulfate, filtered,
and the filtrate was evaporated to dryness in vacuo. The residue
was recrystallized from benzene to give 6.997 g. (93%) of 3-benzyl-
2-naphthamide (53), m.p. 197.5-198°C.

**Anal.** Calcd. for C₁₈H₁₅NO (261.3): C, 82.73; H, 5.79; N, 5.36.

**Found:** C, 82.84; H, 5.93; N, 5.52.

3-Benzyl-2-cyanonaphthalene (54).—A mixture of amide (53)
(25.2 g.) in phosphorus oxychloride (125 ml.) was heated on the steam
bath for 2.75 hours. The reaction mixture was then poured into ice.
Dilute aqueous sodium carbonate solution was then added and the product
was extracted with methylene chloride. The organic extract was washed
once with dilute aqueous sodium carbonate solution and once with water.
The organic extract was dried over sodium sulfate, filtered, and the
filtrate was evaporated to dryness in vacuo. The residue was chromato-
graphed with benzene on neutral alumina grade III. The slightly
colored eluant was treated with activated charcoal, filtered and
evaporated to dryness in vacuo. The residue was crystallized from
cyclohexane to give 18.214 g. (77.5%) of 3-benzyl-2-cyanonaphthalene
(54) which crystallized simultaneously as needles, m.p. 111-112°C
and as the rhombic form, m.p. 108-111°C.

**Anal.** Calcd. for C₁₈H₁₅NO (261.3): C, 82.73; H, 5.79; N, 5.36.

**Found:** C, 82.84; H, 5.93; N, 5.52.

3-Benzyl-2-benzoylnaphthalene (55).—A solution of nitrile (54)
(15.855 g., 0.065 mole) in benzene was added dropwise over a period
of 40 minutes to a refluxing solution of phenylmagnesium bromide
(0.13 mole) in ethyl ether. After refluxing for 5.5 hours, the excess
Grignard reagent was decomposed with water. Dilute hydrochloric acid
was then added to the stirred reaction mixture. The dilute acid dissolved all the inorganic salts and at the same time the imine hydrochloride precipitated. The product was removed by filtration, dried and washed with Skelly F to give the crude imine hydrochloride, m.p. 250-257°. The imine hydrochloride was then heated in ethanol-dilute hydrochloric acid on the steam bath for 4 days. The reaction mixture was cooled and the product was extracted with methylene chloride. The extract was reduced in volume, treated with activated charcoal, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was chromatographed with carbon tetrachloride on neutral alumina grade III. The eluant was evaporated to dryness in vacuo and the residue was crystallized from cyclohexane to give 14.502 g. (69%) of 3-benzyl-2-benzoylnaphthalene (55), m.p. 82-83°. An additional 2.9 g. was obtained from the mother liquor.

Anal. Calcd. for C_{24}H_{18}O (322.4): C, 89.41; H, 5.63.

Found: C, 89.09; H, 5.89.

2,3-Dibenzynaphthalene (25).--Aluminum chloride (2.03 g., 0.015 mole) in ethyl ether (100 ml.) was added to a mixture of lithium aluminum hydride (0.265 g., 0.007 mole) in ethyl ether (100 ml.). A solution of ketone (55) (1.13 g.) in ethyl ether (50 ml.) was added dropwise over a period of 5 minutes to the reducing complex. After refluxing for 1 hour, the reaction mixture was hydrolyzed by adding moist ether, followed by water and finally by dilute hydrochloric acid. The organic phase was separated and the aqueous layer was extracted twice with ethyl ether. The combined organic extract was dried over sodium sulfate, filtered, and the filtrate evaporated to dryness.
in vacuo. The residue was chromatographed with methylene chloride on neutral alumina grade I. The solvent was removed in vacuo and the residue was crystallized from benzene-ethanol to give 0.876 g. (81%) of 2,3-dibenzynaphthalene (25), m.p. 124-125°. UV-spectrum (cyclohexane): λ max (log ε) 232 (5.11); 269 (3.79); 279 (3.73).

Anal. Calcd. for C₃₄H₂₈O₂: C, 93.46; H, 6.54.

Found: C, 93.51; H, 6.57.

**Attempted Monobromination of 3-Benzyl-2-benzoylnaphthalene (55).**—
To a stirred solution of ketone (55) (0.506 g.; 1.57 millimole) in carbon tetrachloride (10 ml.), which was irradiated with a General Electric sunlamp, was added over a period of one hour, 4.6 ml. of carbon tetrachloride containing 0.252 g. (1.58 millimole) of bromine. After stirring for an addition half-hour, the solvent was removed in vacuo and the residue was crystallized from ethyl ether to give 0.202 g. (75% based on bromide) of 2,3-dibenzoylnaphthalene, m.p. 138-142°, obtained in three crops. The unreacted ketone (55) was not isolated.

**trans-1,2-Diphenynaphtho[b]cyclobutene (44) from 3-Benzyl-2-benzoylnaphthalene (55).**—A mixture of ketone (55) (5.121 g.) and sodium borohydride (2.081 g.) in absolute ethanol (80 ml.) was refluxed for 6.5 hours. After cooling to room temperature, 10% aqueous sodium hydroxide solution (100 ml.) and water (75 ml.) was added. The product was extracted with benzene, and the extract was washed with water, dried over sodium sulfate and filtered. The filtrate was evaporated to dryness in vacuo to give the alcohol (56) as an oil which solidified on standing, m.p. 102-104°. The alcohol (56) was cooled in an ice-salt bath and thionyl chloride (33 ml.), cooled to 0°, was added. The
mixture was swirled and allowed to come to room temperature. After all the alcohol went into solution, the excess thionyl chloride was removed in vacuo. The resulting oil was washed three times with 35-ml. portions of Skelly F. The solvent was evaporated to dryness in vacuo after each washing. To the resulting oily chloride (57) was added t-butyl alcohol (75 ml.) containing a large excess of potassium t-butoxide (8-10 g.). The mixture was refluxed for 2 hours on the steam bath. After cooling, the reaction mixture was poured into dilute acetic acid. The aqueous solution was extracted 4 times with benzene. The benzene extract was washed once with water, followed by dilute aqueous potassium carbonate solution and once again with water. The organic extract was dried over sodium sulfate, filtered and the filtrate was evaporated to a smaller volume in vacuo. The benzene solution was then treated with activated charcoal, filtered, and the filtrate evaporated to dryness in vacuo. The residue was recrystallized from methylene chloride-Skelly B to give 3.795 g. (80%) of trans-1,2-diphenylnaphtho[b]cyclobutene (44), m.p. 158-160° obtained in two crops. Recrystallization from Skelly F gave a sample, m.p. 158-159°. UV-spectrum (cyclohexane): λmax (log ε), 230 (4.96); 261 (3.70); 270 (3.78); 280 (3.79); 292 (3.66); 306 (3.19); 320 μμ (3.31).

A sample of alcohol (56) from another run was dissolved in methylene chloride, treated with activated charcoal, and filtered. Crystallization from methylene chloride-Skelly B gave the analytical sample, m.p. 113-114°.

Anal. Calcd. for C_{24}H_{20}O (324.4): C, 88.85; H, 6.21.

Found: C, 88.73; H, 6.28.
1,2-Dibromo-1,2-diphenylnaphtho[b]cyclobutene (59).—To a mixture of cyclobutene (44) (0.291 g., 0.95 millimole) and finely ground N-bromosuccinimide (0.395 g., 2.22 millimole) in carbon tetrachloride (10 ml.) was added benzoyl peroxide (0.050 g.) in chloroform (0.5 ml.). The reaction mixture was refluxed for 1 hour. After cooling to room temperature, the mixture was filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from methylene chloride-Skelly B to give 0.307 g. (70%) of 1,2-dibromo-1,2-diphenylnaphtho[b]cyclobutene (59), m.p. 180-183° dec. Recrystallization from methylene chloride-petroleum ether, b.p. 30-60°, gave the analytical sample, m.p. 185-186° dec.

Anal. Calcd. for C_{24}H_{16}Br_{2} (464.1): C, 62.10; H, 3.47; Br, 34.43.

Found: C, 61.97; H, 3.45; Br, 37.24, 33.28.

1,2-Diphenylnaphtho[b]cyclobutadiene (20).—To a warm solution of the 1,2-dibromide (59) (0.139 g.) in benzene (15 ml.) was added zinc dust (2.5 g.). The reaction mixture was swirled and heated on the steam bath for 2-3 minutes. The reaction mixture was filtered and the filtrate was chromatographed with benzene on neutral alumina grade I. The benzene eluant was evaporated to dryness in vacuo and the residue was taken up in a minimum amount of benzene. The addition of a small amount of 2,4,7-trinitrofluorenone (TNF) to the benzene solution followed by crystallization from benzene-methanol gave 0.056 g. (30%) of the TNF complex of 1,2-diphenylnaphtho[b]cyclobutadiene obtained as black needles, m.p. 183-185°. A benzene solution of the TNF complex was chromatographed on neutral alumina grade I. The eluant was evaporated to dryness in vacuo and the residue was recrystallized.
from hexane to give the pure cyclobutadiene (20) as bright red needles, m.p. 136-137°.

A mixture of the dibromide (59) (0.073 g.) and sodium iodide (0.239 g.) in acetone (6 ml.) was heated on the steam bath for 3 minutes. The mixture was then chromatographed with acetone on neutral alumina grade I. The acetone eluant was evaporated to dryness in vacuo and the residue was taken up in benzene. A small amount of TNF was added. Crystallization from benzene-methanol gave 0.019 g. of the TNF complex. A benzene solution of the complex was decomposed on neutral alumina grade I to give, after crystallization from hexane, 0.008 g. (16%) of the cyclobutadiene (20).

The cyclobutadiene (20) obtained in these reactions is identical to the material first prepared by B. Hwang.

The Addition of Bromine to 1,2-Diphenylnaphtho[b]cyclobutadiene (20).—To a solution of the cyclobutadiene (20) (0.011 g.) in carbon tetrachloride (5 ml.), cooled to 0°, was added 1.1 ml. of carbon tetrachloride containing 0.0058 g. (1 equivalent) of bromine. The solution was decolorized instantaneously. The solvent was removed in vacuo to give the dibromide (59), m.p. 175-176° dec. The infrared spectrum of this material was identical to the dibromide obtained from trans-1,2-diphenylnaphtho[b]cyclobutene (44) and N-bromosuccinimide. Recrystallization from methylene chloride-hexane gave the pure dibromide (59), m.p. 182-183° dec.

Adduct (63) from 3-Sulfolene (62) and 1,4-Diphenyl-2,3-benzofuran.—A mixture of 1,4-diphenyl-2,3-benzofuran (14.14 g.) and 3-sulfolene (21.31 g.) in benzene (140 ml.) was refluxed for 64 hours. After
cooling to room temperature, the product was removed by filtration and the filtrate was evaporated to dryness in vacuo. The solid material was combined and suspended in water. The mixture was heated on the steam bath to dissolve the excess 3-sulfolene. The product was then filtered, washed with water, and air dried to give 19.77 g. (97%) of adduct (63), m.p. 223-264° dec. Recrystallization from benzene-Skelly B gave the analytical sample, m.p. 257-287°.

**Anal. Calcd. for C\textsubscript{24}H\textsubscript{20}SO\textsubscript{3} (388.4):**

C, 74.21; H, 5.19; S, 8.24.

**Found:** C, 74.32; H, 5.11; S, 8.14.

**4,9-Diphenyl-1,3-dihyronaphtho[2,3-c]thiophene-2,2-dioxide (64).**

A mixture of adduct (63) (13.503 g.) in glacial acetic acid (110 ml.) and 48% hydrobromic acid (20 ml.) was heated on the steam bath for 7 hours. The mixture was then allowed to stand at room temperature for 12 hours. The mixture was poured into water and the product was removed by filtration and air dried to give 12.268 g. (94%) of sulfone (64), m.p. 301-302°. Chromatography with methylene chloride on acid washed alumina grade III followed by crystallization from methylene chloride-hexane gave the analytical sample, m.p. 301-302°.

**Anal. Calcd. for C\textsubscript{24}H\textsubscript{18}SO\textsubscript{2} (370.4):**

C, 77.82; H, 4.90; S, 8.64.

**Found:** C, 77.27; H, 4.94; S, 8.82.

**3,8-Diphenylnaphtho[b]cyclobutene (15).**

A solution of sulfone (64) (6.710 g.) in diethyl phthalate (93 ml.) was refluxed for 5 hours and 20 minutes. After cooling, the reaction mixture was poured into 15% aqueous sodium hydroxide solution (200 ml.). Ethanol (150 ml.) was added and the mixture was warmed on the steam bath until the diethyl phthalate was saponified. The saponification may occur
rapidly within a few minutes or it may require several hours of heating. After cooling to room temperature, the product was extracted with benzene. The benzene extract was washed with aqueous ammonium chloride solution, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was chromatographed with chloroform on acid washed alumina grade II. The chloroform eluant was evaporated to dryness in vacuo and the residue was chromatographed with benzene on neutral alumina grade I. The benzene eluant was evaporated to dryness in vacuo and the residue was crystallized from methylene chloride-Skelly B to give 3.177 g. of 3,8-diphenyl-naphtho[b]cyclobutene (15), m.p. 207-208° (lit.16 m.p. 201-202°). The infrared spectrum of this material is in agreement with that recorded in the literature.16 UV-spectrum (cyclohexane): $\lambda_{\text{max}}$ (log ); 232 (4.65); 235 (4.64); 307 m\(\mu\) (4.16). Lit.17 (cyclohexane): $\lambda_{\text{max}}$ (log ); 232 (4.65); 239 (4.61); 308 m\(\mu\) (4.19).

The column was then eluted with chloroform-methanol. This fraction was evaporated to dryness in vacuo. The residue was taken up in methylene chloride, treated with activated charcoal, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from benzene-Skelly B to give 1.747 g. (26%) of recovered sulfone (64), m.p. 301-302°. The yield of the cyclobutene (15) based on unrecovered sulfone was 77%.

Irradiation of 4,9-Diphenyl-1,3-dihydronaphtho[2,3-c]thiophene-2,2-dioxide (64).—A solution of sulfone (64) (0.166 g.) in reagent grade benzene (175 ml.) was irradiated using a Hanovia medium pressure
lamp model #6798 (quartz probe) for 17 hours at 8°. The solvent was removed in vacuo and the residue was taken up in methylene chloride, treated with activated charcoal, and filtered. Crystallization from methylene chloride-benzene gave 0.132 g. (79.5%) of recovered sulfone (64), m.p. 301-302°, obtained in two crops.
PART II
THE SYNTHESIS AND REACTIONS OF STABILIZED
2,3-NAPHTHOQUINONOID SYSTEMS

I. Introduction

During the work-up of the reaction product from the lactone (36) and phenylmagnesium bromide under strongly acid conditions, an intense red fluorescent color was observed. It was thought that the red color might be due to the acid catalyzed elimination of water from the lactol (37) to form 1,3-diphenynaphtho[2,3-c]furan (65). The analogous reaction of lactol (66) with acid to give 1,4-diphenyl-2,3-benzofuran (9) is well known. The work reported here concerns the isolation and reactions of the naphthofuran (65).

\[
\text{(36)} \quad \text{1) } \phi \text{Mg Br} \quad \text{2) } H^+ \quad \rightarrow \text{(37)} \quad \rightarrow \text{(65)}
\]

\[
\phi \text{OH} \quad \text{ (66)} \quad \rightarrow \quad \phi \text{C} \quad \phi \text{ (9)}
\]

The naphthofuran (65) may be considered as an analogue of the unknown 2,3-naphthoquinone. No stable compounds containing the

\[\text{L. F. Fieser, J. Am. Chem. Soc., 52, 5218 (1930).}\]
2,3-naphthoquinonoid system have been previously described. Wittig\textsuperscript{45} has prepared N-methyl isoindole (68) in 74\% yield by treating 2,2-dimethyl isoindolinium bromide (67) with phenyl lithium in ether. The isoindole (68) undergoes the Diels-Alder reaction with maleic anhydride to form the adduct (69). Wittig\textsuperscript{46} attempted to extend this reaction to the preparation of a 2,3-naphthoquinonoid system, viz. N-methyl 5,6-benzisoindole (72). The treatment of 2,2-dimethyl-5,6-benzisoindolinium bromide (70) with phenyllithium resulted in the formation of 1,2-dimethyl-5,6-benzisoindoline (71) in 45\% yield. In addition, methane was evolved to the extent of 50\% of the theory which corresponds to the formation of (72). The N-methyl-5,6-benzisoindole (72), if formed, could not be isolated or even trapped with maleic anhydride.

\[
\begin{align*}
\text{(67)} & \xrightarrow{\Phi Li} \text{(68)} \xrightarrow{\text{C}} \text{(69)} \\
\text{(70)} & \xrightarrow{\Phi Li} \text{(71)} \xrightarrow{\text{C}} \text{(72)}
\end{align*}
\]

As is to be expected, the chemistry of 1,3-diphenylnaphtho[2,3-2]-
furan closely parallels the chemistry of 1,4-diphenyl-2,3-benzofuran (9). The benzofuran (9) can be oxidized to o-dibenzoylbenzene.\(^{43}\)

The ability of (9) to act as a diene in the Diels-Alder reaction is well documented in the literature. The reaction is usually carried out under relatively mild condition giving adducts which, in some cases, reverse to their precursors with surprising ease. The benzofuran (9) can be converted to the corresponding 1,4-diphenyl-2,3-benzothiophene (73) by reacting with phosphorus pentasulfide.\(^{47}\)

Similarly, the naphthofuran (65) reacts with various dieneophiles, with phosphorus pentasulfide, and is readily oxidized. The results of these reactions will be described in detail in the next section.

The action of light\(^{43}\) or heat\(^{48}\) on 1,4-diphenyl-2,3-benzofuran (9) has been reported to give the dimer formulated as (74). The form of the peroxide (75) is also described.\(^{49}\) The nitration of the benzofuran (9) and the benzothiophene (73) with potassium nitrate in sulfuric acid gives 1-(m-nitrophenyl)-4-phenyl-2,3-benzofuran and thiophene (76), respectively.\(^{50}\)

The dimerization, peroxide formation and the substitution reactions of the naphthofuran (65) were not investigated.

\(^{49}\)C. Dufrasie and S. Ecary, Compt. rend., 223, 735 (1946).
II. Discussion and Interpretation of Results

A solution of excess phenylmagnesium bromide was added to a suspension of the lactone (36) in tetrahydrofuran. The work-up of this reaction mixture with dilute hydrochloric acid gave red fluorescent oils which slowly decolorized on standing. Solutions of the red oil in ethyl ether were decolorized rapidly upon addition of N-phenylmaleimide which suggested the presence of 1,3-diphenylnaphtho[2,3-c]-furan (65), the naphthalene analogue of 1,4-diphenyl-2,3-benzofuran (9). The red material could not be obtained in crystalline form by working up the reaction with dilute hydrochloric acid. This is in contrast to the easy preparation of 1,4-diphenyl-2,3-benzofuran (9) described by Newman\textsuperscript{27} in which the reaction product of 3-phenylphthalide and phenylmagnesium bromide is worked up with dilute hydrochloric acid to give crystalline (9) in 87\% yield.

The work-up of the reaction mixture with aqueous ammonium chloride solution resulted in the isolation of the lactol (37) in 91\% yield. The treatment of the pure lactol (37) with hydrochloric acid gave the same red oils which refused to crystallize.

The fortuitous choice of glacial acetic acid as the dehydrating agent met with success. The naphthofuran (65) could be obtained in the form of dark red crystalline plates simply by heating a mixture of the solid lactol (37) with a small amount of glacial acetic acid on the steam bath for several minutes. The naphthofuran (65) was removed by filtration and washed with Skelly B. All attempts to
recrystallize (65) failed. Solutions of (65) in organic solvents slowly decolorized on standing. The naphthofuran (65) obtained from the glacial acetic acid reaction analyzed reasonably well for C_{24}H_{16}O. The crystalline naphthofuran (65) is stable for several months when stored in the dark and in the absence of air.

The attempted generation of the naphthofuran (65) using formic acid (98-100%) under the same conditions used with glacial acetic acid resulted in the formation of an orange color. No naphthofuran (65) was formed. The same orange color was formed by mixing (65) with formic acid. The orange color was also noticed in the aqueous acid layer from the dilute hydrochloric acid work-up of the Grignard reaction. The formation of the carbonium ion (77) is probably responsible for the orange color.

![Molecules](attachment:image)

The reaction of (65) with phosphorus pentasulfide in carbon disulfide gave the corresponding 1,3-diphenylnaphtho[2,3-c]thiophene (78) isolated as the 2,4,7-trinitrofluorenone complex. Alumina chromatography of the complex afforded the pure thiophene (78) as bright red needles. The crystalline thiophene (78) appears to be stable indefinitely.

The conversion of the benzofuran (9) with phosphorus pentasulfide to the corresponding thiophene (73) has been carried out by Dufraisse.47
Bistrzycki and Brenken⁵¹ had prepared the thiophene (73) some years earlier by treating 2,4,4-triphenyl-1,3-oxathiophanone-5 (79) with concentrated sulfuric acid. These workers, however, gave the incorrect structure (80) to the benzothiophene (75). The work of Dufraisse⁴⁷ clarified this situation.

![Chemical Structures](image)

(79)  (80)

There are two important factors contributing to the stability of the naphthofuran (65) and the naphthothiophene (78). The first results from the interaction of one of the unshared electron pairs of the hetero atom with the naphthoquinonoid system. The resulting system may be considered aromatic in the same way as furan and thiophene are considered aromatic.⁵²

It can be seen by comparing the relative stability of some related o-benzoquinonoid heterocyclic compounds that the major stabilizing factor in (65) and (78) is the phenyl groups in the 1- and 3-positions. The 1,4-diphenyl-2,3-benzothiophene (73) is a very stable crystalline compound.⁴⁷ By contrast, isothianaphthene (82) obtained by the catalytic dehydrogenation of dihydroisothianaphthene (81) is stable for only a few days even when stored under nitrogen at -30°C.⁵³

A similar comparison can be made with N-methyl isoindole (68) and 1,3-diphenyl-2-methyl isoindole (83). The isoindole (68) is decomposed to a brown oil when exposed to the air while the diphenyl derivative (83) is stable to air and light for a long time.

The oxidation of the naphthofuran (65) with pyridine-chromic oxide complex gave 2,3-dibenzoylnaphthalene in 63% yield. The diketone (24) was identical to the material obtained from the oxidation of the lactol (37) (See Part I).

The reaction of the naphthofuran (65) with N-phenylmaleimide in ethyl ether at room temperature gave a 87% yield of adduct (84). A benzene solution of the naphthothiophene (78) and N-phenylmaleimide was allowed to stand at room temperature and in the dark for 22 hours. The formation of a Diels-Alder adduct was not detected.

This same order of reactivity in the Diels-Alder reaction is also found in the related benzofuran (9) and the benzothiophene (73). In fact, in Dufraisse's method of preparing the benzothiophene (73) from (9), the separation of the product from the starting material is based on the rapid Diels-Alder reaction of (9) with maleic anhydride. After the adduct of (9) was removed by extraction with aqueous base, the unreacted benzothiophene (73) was obtained.

The addition of tetracyanoethylene to a benzene solution of the naphthofuran (65) at room temperature gave the adduct (85) in 71% yield.\(^\text{54}\)

\[^{54}\text{W. Theilacker and W. Schmidt, Ann., 605, 43 (1957).}\]
yield. The very reactive tetracyanoethylene also formed an adduct (86) with the naphthothiophene (78) under the same conditions in 83% yield. Benzene solutions of adducts (85) and (86) reverse to their precursors when heated on the steam bath.

Hexafluoro-2-butyne was bubbled through a warm solution of the naphthofuran (65) in benzene. Work-up of the reaction gave adduct (87) in 72% yield.

The addition of excess maleic anhydride to a solution of the naphthofuran (65) in methylene chloride-benzene at room temperature resulted in the instantaneous disappearance of the red color. Adduct (88) was obtained in 84% yield. The adduct (88) dissociates when heated. Recrystallization of the adduct (88) from carbon tetrachloride gave a crystalline addition product composed of the adduct and carbon tetrachloride in a 1:1 mole ratio as determined by the elemental analysis.

The corresponding adduct (89) of the 1,4-diphenyl-2,3-benzofuran (9) and maleic anhydride has been prepared by a number of workers. Weiss and Abeles\(^\text{55}\) have prepared the adduct (89) by warming (9) and maleic anhydride in xylene. Barnett\(^\text{56}\) prepared the adduct at room temperature in ethylene dichloride solution. The adduct (89) dissociates into its components extremely easily which prompted Barnett to make the statement, "this ease of dissociation is remarkable since it must involve the disturbance of the aromatic structure." Dufriasse and Priou\(^\text{57}\) have prepared both the endo and exo isomers of adduct (89).

\(^{55}\)R. Weiss and A. Abeles, Monatsh. Chem., 61, 162 (1932).
Chart VI
Diels–Alder Adducts and Derivatives

(84)  

(85) \(X = \text{O}

(86) \(X = \text{S}

(87)  

(88)  

(90)  

(91)  

(92)  

(93)
The addition of 3-nitrostyrene to the naphthofuran (65) in methylene chloride solution at room temperature gave the adduct (90) in 82% yield. The corresponding adduct of the benzofuran (90) has been prepared by refluxing the reactants in ethanol. \(^{58}\)

The reaction of dimethyl acetylenedicarboxylate and the naphthofuran (65) in benzene at room temperature gave adduct (91) in 77% yield. The reaction was complete within 2-3 minutes. The adduct (91) does not reverse appreciably even at its melting point. Berson \(^{59}\) has prepared the analogous adduct of the benzofuran (9) and dimethyl acetylenedicarboxylate in 84% yield by refluxing the reactants in benzene for 105 minutes.

The reaction of 1,4-naphthoquinone and the naphthofuran (65) in benzene at room temperature, gave after 1-2 minutes, the adduct (92) in 86% yield. Treatment of adduct (92) with hydrobromic acid in glacial acetic acid gave 6,13-diphenylpentacene-5,14-quinone (93) in 48% yield. Bergmann \(^{60}\) has prepared the corresponding adduct (94) of 1,4-diphenyl-2,3-benzofuran (94) and 1,4-naphthoquinone by refluxing the reactants in xylene for 2 hours. The adduct (94) was treated with hydrobromic acid in glacial acetic acid at 37\(^\circ\) for two days to give the naphthacenequinone (95) as the major product. In addition there was obtained a small amount of the tautomeric dihydroxy compound (96). Dufraisse \(^{61}\) prepared the adduct (94) in 90% yield by adding a few drops of chloroform to a mixture of the reactants. Treatment of


\(^{61}\) C. Dufraisse and P. Campagnon, Compt. rend., 207, 585 (1938).
Chart VII

Diels—Alder Adducts and Derivates

(94)  

(95)  

(96)  

(97)  

(98)  

(99)
adduct (94) with sulfuric acid gave the quinone (95) in 70% yield.

The reaction of one mole of benzoquinone with two moles of the naphthofuran (65) in benzene at room temperature gave the bis adduct (97) in 72% yield. An analytical sample of adduct (97) could not be obtained due to the adduct's ease of reversal. Allen and Gates have prepared the corresponding adduct of the benzofuran (9) and benzoquinone by refluxing the reactants in ethanol for 2 hours. Etienne has also prepared the bis adduct in 97% yield by adding a few drops of chloroform to a mixture of the reactants. The reaction was complete within 15 minutes.

The reaction of the naphthofuran (65) with aconaphthylene in benzene at room temperature gave, after 40 minutes, the adduct (98) obtained as colorless crystals. Chromatography on alumina gave a high and a low melting isomer. The total yield of both isomers was 42%. The yield of adduct (98) was increased to 87% by carrying out the reaction in boiling benzene with an excess of aconaphthylene. Treatment of adduct (98) with hydrobromic acid in glacial acid gave the aromatized product (99) in 74% yield. Bergmann has prepared the adduct of the benzofuran (9) and aconaphthylene in quantitative yield by refluxing the reactants in xylene for 7 hours. The adduct obtained is described as yellowish needles with green fluorescence. The color must be due to traces of starting benzofuran (9). Refluxing the adduct

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Chart VIII

Diels–Alder Adducts and Derivatives

(100)

(101)

(102)

(103)

(104)

(105)

(106)

(107)

(108)

(109)
in acetic acid containing hydrobromic acid gave the aromatized product obtained as silvery fluorescent leaflets.

Cava and Pohlke 65 have trapped the transient species benzocyclobutadiene and several of its halogenated derivatives with 1,4-diphenyl-2,3-benzofuran (9). The reaction of trans-1,2-dibromobenzocyclobutene (100) with zinc in boiling ethanol in the presence of (9) gave the adduct (101) in 55% yield. Adduct (101) was treated with hydrochloric acid in ethanol to give 5,10-diphenylbenzo[b]biphenylene (102). The reaction of dibromide (100) with potassium t-butoxide in t-butyl alcohol in the presence of (9) gave a 73% yield of the monobrominated adduct (103).

The use of 1,3-diphenylnaphtho[2,3-c]furan (65) as the trapping agent in a similar series of experiments was investigated.

The reaction of the dibromide (100) and 1,3-diphenylnaphtho-[2,3-c]furan (65) with potassium t-butoxide in benzene gave a 52% yield of the expected adduct (104). No adduct was obtained from the reaction of the dibromide (100) with zinc in the presence of naphthofuran (65). This reaction was carried out only twice and was not investigated in detail.

The reduction of adduct (104) with hydrazine and palladium 66 gave the dehalogenated adduct (105) which corresponds to the Diels-Alder adduct of benzocyclobutadiene and the naphthofuran (65). The reaction of the reduced adduct (105) with polyphosphoric acid (PPA) at 130-170°C

66 W. L. Mosby, Chem. and Ind., 1348 (1959) and references cited therein.
gave, after the work-up, dark brown needles, m.p. 228-231°, which analyzed for C_{32}H_{20} and was assumed to be 5,12-diphenylnaphtho[2,3-b]-biphenylene (106).

Treatment of the reduced adduct (105) with phosphorus pentasulfide in carbon disulfide gave a 61% yield of a hydrocarbon obtained as golden yellow needles, m.p. 228-229°, which analyzed for C_{32}H_{20}. This material was identified as the authentic naphthobiphenylene (106) from its ultraviolet spectrum and from the Diels-Alder adduct (107) obtained in 62% yield by refluxing (106) and N-phenylmaleimide in toluene for 13 days.

The product from the PPA reaction was now reinvestigated. Thin layer chromatography indicated the presence of two compounds which have almost identical R_f values. One component of this mixture was identified as the naphthobiphenylene (106) by comparative thin layer chromatography. The second component was assumed to be 3,6-diphenyl-1,2-benzo-4,5-naphthopentalene (108) which could be formed according to the following mechanism.

\[ (105) \xrightarrow{H^+} \]

\[ \xrightarrow{\text{Diels-Alder}} \]

\[ \xrightarrow{-H^+ \text{ or } H_2O} \]

The hydrocarbon mixture could not be separated by alumina chromatography. The separation of the naphthopentalene (108) was accomplished
by complex formation with 2,4,7-trinitrofluorenone (TNF). Repeated recrystallization of the TNF complex of the mixture gave a single complex which was decomposed with benzene on alumina to give the pure naphthopentalene (108), m.p. 240-242°. A similar mixture of the biphenylene (106) and the pentalene (108) was obtained by heating the reduced adduct (105) with hydrobromic acid in glacial acetic acid.

Indirect evidence for the pentalene structure (108) was obtained by investigating the reaction of polyphosphoric acid on adduct (101) prepared by Cava and Pohlke. In this case, the rearrangement would result in the formation of 3,6-diphenyl-1,2,4,5-dibenzopentalene (109) which could be compared with an authentic sample prepared by the method of K. Brand (see experimental).

The reduction of the bromo adduct (103) with hydrazine and palladium and the subsequent dehydration of the product with phosphorus pentasulfide to the biphenylene (102) were investigated to test the applicability of these reactions.

The reduction of the bromo adduct (103) with hydrazine and palladium gave a 53% yield of the reduced product (101) identical to the product obtained by Cava and Pohlke. Treatment of (101) with phosphorus pentasulfide in carbon disulfide gave the benzobiphenylene (102) in 82% yield.

Heating a mixture of adduct (101) with polyphosphoric acid gave a mixture (32%) of 5,10-diphenylbenzo[b]biphenylene (102) and 3,6-diphenyl-1,2,4,5-dibenzopentalene (109). Attempts to separate the mixture by crystallization, chromatography, or by complex formation

67K. Brand, Ber., 45, 3071 (1912).
with 2,4,7-trinitrofluorenone failed. The identity of the biphenylene (102) and the pentalene (109) was established by the comparison of the infrared spectrum of the mixture with the spectra of the pure compounds, and by comparative thin layer chromatography. The absorption spectrum between 300 mμ and 500 mμ exhibited four maxima. The spectrum of a synthetic mixture of (102) and (109) showed the same four maxima. In the reaction described in the experimental section, the concentration of the pentalene (109) in the mixture amounted to 21%. That the rearrangement to the pentalene (109) does not occur by way of the biphenylene (102) was shown by heating a mixture of (102) in polyphosphoric acid. The biphenylene (102) was recovered unchanged.

The Diels-Alder reaction of 1,3-diphenynaphtho[2,3-c]furan (65) and 3-sulfolene (62) (2,5-dihydrothiophene-1,1-dioxide) was considered. The adduct could serve as the precursor to the synthesis of 3,10-diphenylanthra[b]cyclobutene (112).

The reaction of the naphthofuran (65) with an excess of 3-sulfolene in refluxing benzene gave a quantitative yield of adduct (110). The reaction of this adduct with hydrobromic acid in glacial acetic acid gave 4,11-diphenyl-1,3-dihydroanthra[2,3-c]thiophene-2,2-dioxide (111) in 62% yield. The pyrolysis of the sulfone (111) in refluxing diethyl phthalate for 11 hours resulted in the recovery of 70.5% of starting sulfone in addition to the 3,10-diphenylanthra[b]cyclobutene (112) in 43% yield based on the unrecovered sulfone.
These results can be compared with the synthesis of 3,8-diphenyl-
naphtho[\(p\)]cyclobutene (15) from the corresponding sulfone (64). (see Part I of this dissertation) In this case, after refluxing the sulfone (64) in diethyl phthalate for 5 hours and 20 minutes, 26% of the sulfone (64) was recovered and the 3,8-diphenylnaphtho[\(p\)]cyclobutene (15) was obtained in 77% yield based on recovered sulfone. It is to be expected that the pyrolysis of the naphthalene sulfone (64) should occur with greater ease than the anthracene sulfone (111) due to the higher energy required to disrupt the anthracene system.

The nuclear magnetic resonance spectrum of the anthracyclobutene (112) shows the usual aromatic absorption between \(\tau=2.01\) p.p.m. and \(\tau=2.81\) p.p.m. The sharp peak at \(\tau=6.68\) is attributed to the benzylic protons. For the lack of a better model, the position of the methyl protons in 9-methylanthracene at \(\tau=7.03\) p.p.m. may be cited. The ultraviolet spectrum of (112) is also in agreement with the assigned structure.

III. Experimental

Lactol (37).—The synthesis of lactol (37) is described in Part I of this dissertation.

1,3-Diphenynaphtho[2,3-c]furan (65).—A mixture of lactol (37) (2.35 g.) in glacial acetic acid (25 ml.) was heated on the steam bath and stirred with a glass rod until all of the lactol was converted to the deep red furan. After cooling, the product was removed by filtration, washed with Skelly B, and dried in vacuo to give 1.958 g. (88.5%) of 1,3-diphenynaphtho[2,3-c]furan (65), m.p. 148–154°C; λ\text{\textsubscript{max}}\text{benzene} 367 \text{mÅ} (ε=5700), 383 (5700), 524 (7900), 546 (7900).

All attempts to recrystallize the compound failed.

Anal. Calcd. for C\textsubscript{24}H\textsubscript{16}O (320.4): C, 89.97; H, 5.03.

Found: C, 89.43; H, 5.29.

1,3-Diphenynaphtho[2,3-c]thiophene (78).—A mixture of phosphorus pentasulfide (2.0 g.) in carbon disulfide (100 ml.) was stirred for 1 hour at room temperature. Solid 1,3-diphenynaphtho[2,3-c]furan (65) (0.675 g.) was then added to the mixture. The mixture was stirred at room temperature for 21.5 hours under a nitrogen atmosphere and in the dark. The insoluble material was then removed by filtration and washed with methylene chloride. The filtrate was concentrated to dryness \textit{in vacuo} and the residue was washed with benzene. The benzene washings were concentrated to dryness \textit{in vacuo}. The residue was then chromatographed with benzene on acid washed alumina grade IV. The deep red eluant was concentrated to a smaller volume \textit{in vacuo} and a solution of 2,4,7-trinitrofluorenone in benzene was added.
The complex of 1,3-diphenylnaphtho[2,3-c]thiophene crystallized upon the addition of methanol to give 0.526 g. (38%) of deep purple needles, m.p. 169-171°.

**Anal. Calcd.** for C₁₃H₁₀NS (651.7): C, 68.19; H, 3.25; N, 6.45; S, 4.92.

**Found:** C, 68.16; H, 3.27; N, 6.47; S, 4.93.

Chromatography of a benzene solution of the complex on basic alumina grade II followed by crystallization from ethyl ether gave the pure naphthothiophene (78) obtained as red needles, m.p. 198-202°; λ_max benzene 513 μ (ε=8700).

**Anal. Calcd.** for C_{24}H₁₆S (336.4): C, 85.67; H, 4.80; S, 9.53.

**Found:** C, 85.61; H, 4.88; S, 9.48.

2,3-Dibenzoylnaphthalene (24).—To pyridine (50 ml.), cooled to 0°, was added in small portions and with stirring chromic oxide (4.0 g.) to the resulting slurry was added 1,3-diphenylnaphtho[2,3-c]furan (65) (0.485 g.). The mixture was stirred at room temperature for 2 days. The reaction mixture was then poured into water and the product was extracted with ethyl ether. The ether extract was washed with dilute hydrochloric acid followed by dilute aqueous sodium bicarbonate solution. The organic extract was dried over sodium sulfate, filtered, and the filtrate evaporated to dryness in vacuo. The residue was dissolved in methylene chloride-ethyl ether, treated with activated charcoal, and filtered. The filtrate was evaporated to dryness in vacuo. The residue was crystallized from ethyl ether to give 0.329 g. (63%) of 2,3-dibenzoylnaphthalene (24), m.p. 143-145°. The diketone
(24) is identical to the sample prepared by the oxidation of the lactol (37). (See Part I of this dissertation)

**N-Phenylmaleimide Adduct (84).**—To a magnetically stirred solution of N-phenylmaleimide (0.123 g.) in ethyl ether (15 ml.) at room temperature was added in small portions naphthofuran (65) (0.219 g.). The product crystallized from solution to give 0.293 g. (87%) of adduct (84), m.p. 287-290° dec., obtained as needles. The analytical sample was obtained by recrystallizing from benzene-ethanol.

**Anal.** Calcd. for C_{24}H_{23}NO_{3} (493.5): C, 82.74; H, 4.70; N, 2.84

Found: C, 82.54; H, 4.94; N, 2.82.

**1,3-Diphenylmaleimide Adduct (86).**—To a stirred solution of thiophene (78) (0.009 g.) and N-phenylmaleimide (0.020 g.) in benzene (5 ml.) was allowed to stand at room temperature and in the dark for 22 hours. At the end of this time, thin layer chromatography with benzene on silica gel plates indicated the presence of only starting material.

**Tetracyanoethylene Adduct (85).**—To a stirred solution of 1,3-diphenylmaleimide (24) (0.353 g.) in benzene (25 ml.) at room temperature was added solid tetracyanoethylene in small portions until all the naphthofuran (65) had reacted as indicated by the rapid disappearance of the red color. The solvent was removed in vacuo and the residue was recrystallized from methylene chloride-Skelly B to give 0.353 g. (71%) of adduct (85), m.p. 238-255° dec.

**Anal.** Calcd. for C_{30}H_{16}ON_{4} (448.5): C, 80.33; H, 3.60; N, 12.51.

Found: C, 80.39; H, 3.96; N, 12.52.
Tetracyanoethylene Adduct (86).—The 2,4,7-trinitrofluorenone complex of 1,3-diphenylnaphtho[2,3-g]thiophene (0.929 g.) was chromatographed with benzene on basic alumina grade II. To the resulting thiophene solution was added solid tetracyanoethylene until the red color was discharged. The solvent was removed in vacuo and the residue was crystallized from methylene chloride-Skelly F to give 0.548 g. (83%) of adduct (86), m.p. 268-280°, dec., obtained as plates.

Anal. Calcd. for C₃₀H₁₆₃N₄ (464.5): C, 77.57; H, 3.47; N, 12.06; S, 6.90.
Found: C, 77.40; H, 3.65; N, 11.78; S, 6.84.

Hexafluoro-2-butyne Adduct (87).—Hexafluoro-2-butyne was bubbled through a warmed solution (55-65°) of 1,3-diphenylnaphtho[2,3-g]-furan (65) (0.960 g.) in benzene (100 ml.) until the red color disappeared (approximately 10 minutes). The solution was concentrated to dryness in vacuo and the residue was chromatographed with benzene on acid washed alumina grade III. The eluant was concentrated to dryness in vacuo and the residue was recrystallized from cyclohexane to give 1.043 g. (72%) of adduct (87), m.p. 162-164°, obtained as rosettes.

Found: C, 69.90; H, 3.62; F, 23.36.

Maleic Anhydride Adduct (88).—To a solution of 1,3-diphenylnaphtho[2,3-g]furan (65) (0.566 g.) in 1:1 methylene chloride-benzene (50 ml.) at room temperature was added an excess of solid maleic anhydride. The reaction was over immediately. The excess maleic anhydride was removed by filtration. The filtrate was treated with activated charcoal, filtered, and evaporated to dryness in vacuo. The residue
was recrystallized from methylene chloride-Skelly F to give 0.626 g. (84%) of adduct (68), m.p. 225-253° dec.

**Anal. Calcd. for C_{28}H_{18}O_{4} (418.4): C, 80.37; H, 4.34.**

**Found: C, 80.08; H, 4.63.**

A sample recrystallized from carbon tetrachloride contained one molecule of solvent of crystallization as determined from the elemental analysis. The carbon from the carbon tetrachloride did not appear as carbon dioxide but was passed through the combustion apparatus unchanged.

**Anal. Calcd. for C_{28}H_{18}O_{4}Cl_{4} (572.3): C, 58.77; H, 3.17.**

**Found: C, 58.70; H, 3.18.**

**β-Nitrostyrene Adduct (90).**—To a solution of 1,3-diphenynaphtho-[2,3-ε]furan (65) (3.566 g.) in methylene chloride (50 ml.) at room temperature was added an excess of β-nitrostyrene. The reaction was complete within several minutes. The solution was concentrated to a smaller volume on the steam bath. The product crystallized upon the addition of Skelly B to give 3.293 g. (82%) of adduct (90), m.p. 243-253° dec. Recrystallization from methylene chloride-Skelly B gave the analytical sample, m.p. 242-255° dec., obtained as prisms.

**Anal. Calcd. for C_{32}H_{23}NO_{3} (469.5): C, 81.86; H, 4.94; N, 32.23**

**Found: C, 81.54; H, 5.07; N, 3.88.**

**Dimethyl Acetylenedicarboxylate Adduct (91).**—A solution of dimethyl acetylenedicarboxylate (0.124 g.) in benzene (25 ml.) was added to 1,3-diphenynaphtho[2,3-ε]furan (65) (0.204 g.). The reaction was stirred for 203 minutes at room temperature to complete
the reaction. The solvent was removed in vacuo and the residue was recrystallized from chloroform-methanol to give 0.277 g. (77%) of adduct (91), m.p. 234-238°.

**Anal.** Calcd. for C_{30}H_{22}O_5 (462.48): C, 77.91; H, 4.80.

Found: C, 77.81; H, 4.88.

**1,4-Naphthoquinone Adduct (92).** —To a solution of 1,4-naphthoquinone (0.283 g.) in benzene (10 ml.) at room temperature was added 1,3-diphenylnaphtho[2,3-g]furan (65) (0.517 g.). The mixture was stirred for 1-2 minutes to complete the reaction. Skelly B was added and the product precipitated to give 0.668 g. (86%) of adduct (92), m.p. 186-203° dec. A sample was dissolved in methylene chloride, treated with activated charcoal, filtered, and crystallized from methylene chloride-Skelly B to give the analytical sample obtained as white needles, m.p. 198-203° dec.

**Anal.** Calcd. for C_{34}H_{22}O_3 (478.5): C, 85.33; H, 4.63.

Found: C, 85.30; H, 4.72.

**6,13-Diphenylpentacene-5,14-quinone (93).** —A mixture of adduct (92) (0.246 g.) in glacial acetic acid (10 ml.) and 48% hydrobromic acid (4 ml.) was heated on the steam bath for 12 hours. The reaction mixture was cooled to room temperature. Water was then added and the product was removed by filtration and air dried. The product was dissolved in methylene chloride, treated with activated charcoal, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was recrystallized from Skelly B to give 0.113 g. (48%) of 6,13-diphenylpentacene-5,14-quinone (93), m.p. 330-332°, obtained as
yellow-orange needles. Recrystallization from benzene-Skelly B gave the analytical sample, m.p. 331-332°.

**Anal. Calcd. for C₃₄H₂₀O (460.5):** C, 88.67; H, 4.38.

**Found:** C, 88.85; H, 4.22.

**Benzquinone Bis Adduct (97).**—A mixture of 1,3-diphenylnaphtho-[2,3-α]furan (65) (0.0036 mole, 1.155 g.) and benzoquinone (0.0018 mole, 0.196 g.) in benzene (20 ml.) was stirred at room temperature for 2-3 minutes. The product crystallized upon the addition of Skelly B to give 0.972 g. (72%) of the bis adduct (97), m.p. 248-258° dec. An analytical sample was not obtained because of the adduct's ease of reversal.

**Anal. Calcd. for C₅₄H₃₆O₄ (748.9):** C, 86.61; H, 4.85.

**Found:** C, 84.76; H, 4.76.

**Acenaphthylene Adduct (98).**—A solution of 1,3-diphenylnaphtho-[2,3-α]furan (65) (1.004 g.) and acenaphthylene (0.530 g.) in benzene (50 ml.) was stirred at room temperature for 40 minutes to complete the reaction. The solution was concentrated to dryness in vacuo and the residue was chromatographed with benzene on neutral alumina grade I. A yellow fraction was collected and evaporated to dryness in vacuo. Hexane was added to the residue to dissolve the unreacted acenaphthylene. Filtration of the mixture gave 0.570 g. of adduct (98), m.p. 262-273° dec. Recrystallization from benzene-hexane gave the analytical sample, m.p. 274-276° dec.

**Anal. Calcd. for C₃₆H₂₄O (472.6):** C, 91.50; H, 5.12.

**Found:** C, 91.16; H, 5.34.
Another benzene fraction was collected from the column. The solvent was removed in vacuo and the residue was crystallized from benzene-hexane to give 0.042 g. of adduct (98), m.p. 225-233° dec. Recrystallization from benzene-hexane gave the analytical sample, m.p. 232-236° dec. The total yield of both isomers was 42%. Both isomers were colorless.

Anal. Calcd. for C_{36}H_{24}O (472.6): C, 91.50; H, 5.12.

Found: C, 91.16; H, 5.16.

The yield of adduct (98) was increased by using a slightly different procedure. Solid naphthofurans (65) (1.13 g.) was added to boiling benzene (30 ml.). Excess acenaphthylene was added rapidly to the boiling solution until the red color was discharged. The reaction was complete within 5 minutes. The reaction mixture was reduced in volume by boiling on the steam bath. The product crystallized upon the addition of hexane. The product was removed by filtration, washed well with hexane and air dried to give 1.46 g. (87%) of adduct (98) obtained as a mixture of isomers, m.p. 214-224° dec.; 265-268° dec.

Aromatized Adduct (99).—A mixture of adduct (98) (unseparated isomers) (0.199 g.) in glacial acetic acid (10 ml.) and 48% hydrobromic acid (2.5 ml.) was heated on the steam bath for 19.5 hours. After cooling to room temperature, water was added and the product was removed by filtration to give 0.184 g. (96%) of aromatized adduct (99), m.p. 270-274°. Recrystallization from methylene chloride-hexane gave the analytical sample, m.p. 273-274°.

Anal. Calcd. for C_{36}H_{22} (454.5): C, 95.12; H, 4.88.

Found: C, 94.87; H, 4.97
1-Bromobenzocyclobutadiene Adduct (104).—To a large excess of potassium t-butoxide in benzene (25 ml.) at room temperature was added 1,3-diphenynaphtho[2,3-g]furan (65) (1.5 g.) and trans-1,2-dibromo-benzocyclobutene (1.494 g.). The mixture was stirred for 5-6 minutes to complete the reaction. The reaction mixture was then poured into water and the product was extracted with benzene. The benzene extract was dried over sodium sulfate, filtered and the filtrate was evaporated to dryness in vacuo. The residue was chromatographed with cyclohexane on neutral alumina grade III. The eluant was evaporated to dryness and the residue was recrystallized from cyclohexane to give 1.213 g. (52%) of adduct (104), m.p. 233-234°. Recrystallization from benzene-Skelly B gave the analytical sample, m.p. 233-236°.

**Anal. Calcd. for C_{32}H_{21}BrO (501.4):** C, 76.67; H, 4.22; Br, 15.94.

**Found:** C, 76.74; H, 4.55; Br, 16.19.

Reduction of Adduct (104).—To a solution of adduct (104) (4.842 g.) in warm benzene (100 ml.) was added absolute ethanol (100 ml.), 5% palladium on carbon (2.2 g.), and 85% hydrazine hydrate (33 ml.). After refluxing for 15 minutes on the steam bath, the reaction mixture was filtered through a celite pad. The filtrate was evaporated to dryness in vacuo. The residue was then dissolved in benzene and water. The benzene layer was separated, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was recrystallized from cyclohexane to give 3.652 g. (90%) of reduced adduct (105), m.p. 185-190°, obtained in two crops. Repeated recrystallization from cyclohexane failed to give an analytical sample.
5,12-Diphenyl[2,3-b]biphenylene (106).—A mixture of reduced
adduct (105) (0.156 g.) in phosphorus pentasulfide (1.5 g.) in carbon
disulfide (30 ml.) was stirred with a magnetic stirring bar for 70
hours at room temperature. The reaction mixture was then evaporated
to dryness in vacuo and the residue was washed with benzene. The
benzene washings were evaporated to dryness and the residue was
chromatographed with benzene on acid washed alumina grade III. The
benzene eluate was evaporated to dryness in vacuo and the residue was
crystallized from benzene-Skelly B to give 0.091 g. (61%) of 5,12-
diphenyl[2,3-b]biphenylene (106), m.p. 228-229° obtained as
golden yellow needles.

\[
\text{\text{\textit{cyclohexane}}} \quad \text{302 m}\mu (\text{log } 4.96), 324 (4.77).
\]

N-Phenylmaleimide Adduct (107).—A solution of 5,12-diphenyl-
naphtho[2,3-b]biphenylene (106) (0.309 g.) and N-phenylmaleimide
(0.245 g.) in toluene (100 ml.) was refluxed for 13 days. The solvent
was removed in vacuo and the residue was dissolved in a small amount
of benzene and placed on a column of neutral alumina grade III. The
column was then eluted with 1:3 benzene-cyclohexane to remove the
unreacted hydrocarbon. Elution with benzene, followed by evaporation
of the solvent in vacuo, and crystallization from chloroform-methanol
gave 0.271 g. (62%) of the yellow adduct (107), m.p. 291-293.
Polyphosphoric Acid on Reduced Adduct (105).—A stirred mixture
of reduced adduct (105) (1.125 g.) in polyphosphoric acid (75 ml.) was
heated between 130 and 170° for 3 hours. After cooling, the reaction
mixture was poured into water and the product was extracted with ben-
zene. The organic extract was washed with dilute aqueous sodium
bicarbonate solution, dried over sodium sulfate, filtered, and the
filtrate was evaporated to dryness in vacuo. The residue was
chromatographed with benzene on neutral alumina grade III. The eluant
was evaporated to dryness in vacuo and the residue was crystallized
from benzene–Skelly B to give 0.631 g. (59%) of dark brown (almost
black) needles, m.p. 228-231°.

Anal. Calcd. for C₁₂₂₂O₉₅₂; H, 4.98.
   Found: C, 94.79; H, 4.99.

The results of thin layer chromatography of the above needles
with carbon tetrachloride on silica gel plates indicated the presence
of two compounds with very similar R_f values. One compound was identi-
fied as 5,12-diphenylnaphtho[2,3-b]biphenylene (106). A sample of the
mixture was dissolved in benzene and the 2,4,7-trinitrofluorenone com-
plex was prepared. Repeated recrystallization from benzene gave a
complex, m.p. 246-247°, which on decomposition on neutral alumina
grade I with benzene followed by crystallization from petroleum ether
gave the pure naphthopentalene (108), m.p. 240-242°, obtained as brown
needles, λ(Cyclohexane) max 275 μ (log 4.74), 320 (4.69), 441 (4.07),
470 (4.10).
Reduction of 1-Bromobenzocyclobutadiene Adduct (103).—To a solution of adduct (103) (0.265 g.) in 1:1 benzene-absolute ethanol (40 ml.) was added 85% hydrazine hydrate (12 ml.) and 5% palladium on carbon (0.6 g.). The mixture was refluxed for 15 minutes on the steam bath and then filtered through a celite pad. The solvent was removed in vacuo and the residue was dissolved in benzene and water. The organic layer was separated, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from petroleum ether, (b.p. 30-60°) to give 0.116 g. (53%) of reduced adduct (101), m.p. 172-175°. Recrystallization from petroleum ether gave a sample, m.p. 195-197°, (lit.65 m.p. 200-202°). The infrared spectrum of this sample was identical to that of the authentic material.65

5,10-Diphenylbenzo[b]biphenylene (102).—A mixture of adduct (101) (0.156 g.) and phosphorus pentasulfide (1.7 g.) in carbon disulfide (30 ml.) was stirred at room temperature for 4 days. The inorganic material was removed by filtration and the filtrate was evaporated to dryness in vacuo. The residue was then washed with methylene chloride. The organic washings were chromatographed on a column of acid washed alumina grade III. Evaporation of the solvent and recrystallization from cyclohexane gave 0.122 g. (82%) of 5,10-diphenylbenzo[b]biphenylene, m.p. 220-222°, (lit.65 m.p. 218-220°). $\lambda_{\text{max}}$ in dioxane 378 m\(\mu\) (log ε 3.55), 400 (3.47).

Polyphosphoric Acid on Adduct (101).—To a solution of adduct (101) (0.323 g.) in methylene chloride (3 ml.) was added polyphosphoric acid (50 ml.). The magnetically stirred mixture was heated slowly to
140° over a period of 1 hour and 20 minutes. After an additional 3 hours at 125°-150°, the reaction mixture was cooled to room temperature, poured into water, and the product was extracted with benzene. The organic extract was washed with dilute aqueous sodium bicarbonate solution, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from cyclohexane to give 0.162 g. (32%) of homogeneous dark brown crystals, m.p. 228-235°. Thin layer chromatography with carbon tetrachloride on silica gel plates indicated the presence of two compounds. These compounds were identified as 5,10-diphenylbenzo[b]biphenylene (102) and 3,6-diphenyl-1,2,4,5-dibenzopentalene (109) by comparison of the infrared spectrum of the mixture with the spectra of the known compounds and by comparative thin layer chromatography on silica gel plates (see below for synthesis of 109). The spectrum between 300 mμ and 500 mμ contained four maxima: λmax dioxane 378 mμ, 400, 423, 447. A similar spectrum was obtained from a mixture of the pure compounds. Attempts to separate the mixture by crystallization, chromatography, or by complex formation with 2,4,7-trinitrofluorenone failed.

An estimate of the per cent composition of the benzopentalene (109) in the mixture was obtained from the absorption spectrum in the 300-500 mμ range. Since there is very little, if any absorption for 5,10-diphenylbenzo[b]biphenylene beyond 325 mμ, the max at 447 mμ for the benzopentalene (109) was used to determine its concentration in the sample from the above reaction.

A solution of the mixture containing 0.0744 g. per liter of dioxane was used for the spectrum. The optical density at 447 mμ was 0.684.
Concentration of (109) in the mixture =

$$\frac{O.D. \times M.W.}{1.53 \times 10^4} = \frac{0.684 \times 354.5}{0.0158 \text{ g./l.}}$$

where: O.D. = optical density

M.W. = molecular weight of (109)

= extinction coefficient of (109)

% of pentalene (109) = \(\frac{0.0158 \text{ g./l.}}{0.074 \text{ g./l.}}\) = 21%

To test the accuracy of this procedure, a sample containing 0.0079 g. of pentalene (109) and 0.05 g. of biphenylene (102) per liter of dioxane was prepared. The optical density at max 447 m\(\mu\) for this solution was 0.345.

Conc. of pentalene (109) = \(\frac{0.345 \times 354.5}{1.53 \times 10^4}\) = 0.0080 g./l.

Reaction of Polyphosphoric Acid on 5,10-Diphenylbenzo[b]biphenylene (102).--To a solution of 5,10-diphenylbenzo[b]biphenylene (102) (0.117 g.) in methylene chloride (2 ml.) was added polyphosphoric acid (25 ml.). The resulting magnetically stirred mixture was heated to 160°-20° for 10.5 hours. After cooling, the reaction mixture was poured into water and the product was extracted with benzene. The organic extract was washed with dilute aqueous sodium bicarbonate solution, dried over sodium sulfate, and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from cyclohexane to give 0.086 g. (74%) of starting material, m.p. 217-219°, (lit., 65 218-220°). The absence of pentalene (109) was confirmed by the examination of the absorption spectrum in the 300-500 m\(\mu\) range.
3,6-Diphenyl-1,2,4,5-dibenzopentalene (109).—The method of K. Brand was used for the synthesis of (109). A solution of diphenylsuccindan-9,12-dione (0.410 g.) in hot benzene was added slowly to an excess of phenylmagnesium bromide in ethyl ether. After refluxing for 8 hours, the reaction mixture was poured into aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with benzene-ethyl ether. The combined extracts were dried over sodium sulfate and filtered. The filtrate was evaporated to dryness in vacuo and the residue was crystallized from ethyl acetate-Skelly B to give 0.484 g. (71%) of 9,10-diphenyldiphansuccindan-9,12-diol, m.p. 243-245° (lit., m.p. 232-234°). The diol (0.454 g.) in glacial acetic acid (12.5 ml.) and formic acid (8 ml.) was heated on the steam bath for 17.5 hours. After cooling to room temperature, the product was removed by filtration and washed with absolute ethanol to give 0.324 g. (79%) of 3,6-diphenyl-1,2,4,5-dibenzopentalene (109), m.p. 259-260° (lit., m.p. 259-260°), \( \lambda_{\text{max}}^{\text{dioxane}} \) 423 m\( \mu \) (log \( e \)=4.18), 447 (4.18).

3-Sulfolene Adduct (110).—A mixture of 1,3-diphenylnaptho[2,3-c]-furan (65) (7.534 g.) and excess 3-sulfolene (20 g.) in benzene (140 ml.) was refluxed for 25 minutes. The resulting light red solution was cooled to room temperature. During this time, the solution became yellow in color. The solvent was removed in vacuo. Water was added to the crystalline residue and the mixture was heated on the steam bath. The organic material became oily as the excess 3-sulfolene melted. Upon further heating, the 3-sulfolene was dissolved leaving the solid adduct suspended in the water. The product was removed by
filtration and air dried to give 10.6 g. (100% = 10.3 g.) of crude adduct (110), m.p. 252-265° dec. Recrystallization from benzene-Skelly B gave the analytical sample, m.p. 314-315° dec.

**Anal.** Calcd. for C_{26}H_{22}SO_{3} (438.5): C, 76.70; H, 5.06; S, 7.30.

**Found:** C, 76.87; H, 5.47; S, 7.06.

4,11-Diphenyl-1,3-dihydroanthra[2,3-c]thiophene-2,2-dioxide (111) —

A mixture of adduct (110) (5.278 g.) in glacial acetic acid (75 ml.) and 48% hydrobromic acid (15 ml.) was heated on the steam bath for 12.5 hours. The reaction mixture was then poured into water and the product was removed by filtration and air dried. The product was dissolved in benzene, treated with activated charcoal, and filtered. Crystallization from benzene-Skelly B gave 4.159 g. (82%) of sulfone (111), m.p. 288-289°. Recrystallization from benzene-Skelly B gave the analytical sample, m.p. 288-289°.

**Anal.** Calcd. for C_{26}H_{20}SO_{2} (420.4): C, 79.98; H, 4.79; S, 7.61.

**Found:** C, 79.85; H, 4.92; S, 7.55.

3,10-Diphenylanthra[b]cyclobutene (112) — A solution of sulfone (111) (3.739 g.) in diethyl phthalate (150 ml.) was refluxed for 11 hours. After cooling to room temperature, the reaction mixture was poured into a hot solution of sodium hydroxide (200 g.) in water (350 ml.) contained in a 3-liter beaker. Ethanol was added to the mixture to aid solution of diethyl phthalate. At this point the vigorous hydrolysis of the diethyl phthalate occurred. After cooling to room temperature, the reaction mixture was extracted with benzene. The benzene extract was dried over sodium sulfate, filtered, and the filtrate was evaporated to dryness in vacuo. The residue was
chromatographed with benzene on neutral alumina grade I. A yellow benzene fraction was collected and evaporated to dryness in vacuo.

Crystallization from methylene chloride-Skelly B gave 0.406 g. of 3,10-diphenylantra[b]cyclobutene (112), m.p. 271-272°. Recrystallization from methylene chloride-Skelly B gave the analytical sample, m.p. 280-282°. λcyclohexane 214 μ (log =4.58), 261 (5.01), 373 (4.02).

**Anal. Calcd. for C_{26}H_{22} (356.4):** C, 94.34; H, 5.66.

**Found:** C, 94.06; H, 5.76.

The column was then eluted with chloroform-methanol. The solvent was evaporated to dryness in vacuo and the residue was recrystallized from benzene-Skelly B to give 2.638 g. (70.5%) of starting sulfone (111), m.p. 284-287°. The yield of (112) based on unrecovered sulfone was 43%.
APPENDIX I: ATTEMPTED SYNTHESIS OF
9,10-PHENANTHROCYCLOBUTENE

The attempted synthesis of 9,10-phenanthrocylobutene (118) by way of the sulfone (116) was carried out during the early stages of this research. The preparation of sulfone (116) is outlined below.

\[
\begin{align*}
\text{(113)} & \rightarrow \text{(114)} & \rightarrow \text{(115)} & \rightarrow \text{(116)} \\
\end{align*}
\]

The pyrolysis of sulfone (116) gave only high melting material which was not identified. Although the cyclobutene (118) could not be obtained under pyrolytic conditions, it was possible to trap the intermediate quinodimethane (117) with N-phenylmaleimide to give the adduct (119) in 25% yield.

\[
\begin{align*}
\text{(118)} & \rightarrow \text{(117)} & \rightarrow \text{(119)} \\
\end{align*}
\]

After this work was completed, two groups of workers have published papers on the preparation and pyrolysis of sulfone (116).\(^69,70\)

The results of these workers are similar to those reported here with the exception of the fact that Stille\textsuperscript{70} has obtained the dimer, 1,2,5,6-bis(9,10-phenathro)cyclooctadiene, m.p. 438-440°, in 21% yield by the pyrolysis of the sulfone (118).

The experimental details for the preparation of sulfone (118) and the adduct (119) obtained by this author are given here.

9,10-Bis(bromomethyl)phenanthrene (114).—The 9,10-dimethylphenanthrene used in this experiment was prepared by the method of Hall.\textsuperscript{71} To a solution of 9,10-dimethylphenanthrene (21.2 g.) in carbon tetrachloride (1 liter) contained in a 2-liter three-neck flask equipped with a reflux condenser, stirring motor and heating mantle was added N-bromosuccinimide (37.6 g.). After heating to reflux, the reaction was initiated benzoyl peroxide in chloroform. After the reaction started, the mixture was refluxed for 2 hours. After standing overnight, the product was removed by filtration. The filtrate was evaporated to dryness \textit{in vacuo} and this residue was combined with the filter cake. The product was washed well with warm water and air dried. Recrystallization from methylene chloride gave 34.6 g. (92.5%) of the dibromide (114), m.p. 237-239°, obtained in three crops. Recrystallization from carbon tetrachloride-Skelly B gave a sample, m.p. 228-230° (lit.,\textsuperscript{72} m.p. 228-229°).

\textsuperscript{72}E. H. Winkelmann, Ph.D. dissertation, Mainz, 1959.
To a mixture of the dibromide (114) (5.0 g., 0.0138 mole) in absolute ethanol (1 liter) was added sodium sulfide (0.041 mole) in absolute ethanol (90 ml.). The reaction mixture was refluxed with stirring for two days. At the end of this time, the solvent was distilled to leave a volume of 350 ml. Water (100 ml.) was then added to the reaction mixture and the product was removed by filtration. The product was chromatographed with methylene chloride on neutral alumina grade I. The eluant was evaporated to dryness to give 2.45 g. (75%) of sulfide (115), m.p. 163-170°. This sulfide is of sufficient purity to be oxidized to the sulfone. The analytical sample was prepared by first forming the mercuric chloride complex in 95% ethanol-benzene solution. The solvent was removed in vacuo and the residue was washed with water. The complex was recrystallized once from benzene-ethanol.

The free sulfide was obtained by bubbling hydrogen sulfide gas through a benzene suspension of the complex. Chromatography with benzene on neutral alumina followed by crystallization from benzene gave the pure sulfide, m.p. 179-183°.

**Anal. Calcd. for C₁₆H₁₂S (236.3): C, 81.34; H, 5.12; S, 13.54.**

**Found: C, 81.46; H, 5.38; S, 13.81.**

To a mixture of sulfide (115) (4.245 g., 0.018 mole) in glacial acetic acid (350 ml.) was added peracetic acid (0.0326 mole). The mixture was heated on the steam bath for 11.5 hours. The solvent was removed in vacuo and the residue was chromatographed with N,N-dimethylformamide on neutral alumina grade I. Crystallization from N,N-dimethylformamide
gave 2.3 g. (52%) of sulfone (116), m. p. 279-283° dec.

**Anal. Calcd. for C₁₆H₁₂SO₂ (268.3):** C, 71.63; H, 4.51; S, 11.93.

**Found:** C, 71.68; H, 4.75; S, 12.13.

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**N-Phenylmaleimide Adduct (119).**—A mixture of sulfone (116) (0.830 g.) and N-phenylmaleimide (1.73 g.) in a 100-ml. round bottom flask was heated in a salt bath at 280° ± 10° for 20 minutes. After cooling to room temperature, the glassy residue was pulverized and washed with benzene. The benzene washings were chromatographed on neutral alumina grade II. The benzene eluant was evaporated to dryness to give 0.295 g. (25%) of adduct (119). Recrystallization from benzene gave the analytical sample, m. p. 230-232°.

**Anal. Calcd. for C₁₆H₁₀NO₂ (377.4):** C, 82.74; H, 5.07; N, 3.71.

**Found:** C, 82.73; H, 5.25; N, 3.69.
APPENDIX II: INFRARED ABSORPTION SPECTRA

The infrared spectra were determined in pressed potassium bromide disks with a Perkin-Elmer, Model 137, Sodium Chloride Spectrophotometer.
Product from
\[ \text{\textcopyright} - C=O \]
and \[ \text{\textcopyright} - CH=CH \]

Figure 1

Figure 2

Figure 3
Figure 16

Figure 17

Figure 18
Figure 22

Figure 23

Figure 24
Figure 28

Figure 29

Figure 30
Figure 46

WAVELENGTH (MICRONS)
APPENDIX III: 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 47