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APPROACHES TO THE SYNTHESIS OF
1,2-DIPHENYL-3,4,5,6-TETRABROMOBENZOYLCYCLOBUTADIENE

DISSERTATION

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

By

Robert Bernard Fechter, B.A.

The Ohio State University
1966

Approved by

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I. INTRODUCTION

In recent years, there have been two areas of chemical research which have emerged into extensive and important fields of study. The first area deals with the problem of aromaticity and its relation to stability in fully unsaturated cyclic molecules. The second area of interest is concerned with strained small-ring molecules. A particular class of compounds which falls under both categories and has attracted the attention of many workers is made up of molecules possessing the cyclobutadiene system.

Cyclobutadiene (1) itself is made up of four sp²-hybridized carbon atoms and therefore possesses a significant amount of strain. It also features a fully conjugated unsaturated cyclic system, thus providing the chemist with an interesting model on which to test the rules of aromaticity.

\[
\begin{align*}
(1) & \quad (1a) & \quad (1b)
\end{align*}
\]

Because 1 does not fit Hückel's rule of having \(4n+2\) \(\pi\) electrons, it is considered to be nonaromatic and, by definition, lacks the high stability usually associated with aromatic molecules. Molecular orbit-
al calculations\(^1,2\) show that there is nearly no resonance interaction between the two double bonds in \(1\). Indeed, \(1\) has recently been generated by Pettit\(^3\) and was found to be a highly reactive transient species. From simple Hückel molecular orbital theory and application of Hund's rule, \(1\) is predicted to have a triplet electronic ground state, as in \(1a\), assuming the carbon atoms occupy the four corners of a square.\(^1\)

More recently, however, Dewar\(^2\) reported making some more elaborate calculations and concluded that \(1\) consists of a rectangular arrangement of atoms and has a singlet electronic ground state as in \(1b\). This theory is strongly supported by the work of Pettit\(^4\) who generated \(1\)

\[\begin{align*}
&\text{Fe(CO)}_3 \quad \text{Ga}^{4+} \\
&\text{(2)} \\
&\text{(1)}
\end{align*}\]

\[\begin{align*}
&\text{CO}_2\text{CH}_3 \\
&\text{CO}_2\text{OH}_3 \\
&\text{H}_2\text{CO}_2\text{O} \\
&\text{CO}_2\text{OH}_3 \\
&\text{CO}_2\text{OH}_3 \\
&\text{CO}_2\text{OH}_3 \\
&\text{CO}_2\text{OH}_3
\end{align*}\]


\(^4\) Ibid., 88, 623 (1966).
from cyclobutadieneiron tricarboxyl (2) and found it to react both as a diene and a dienophile in a stereospecific manner.

As a result of the instability of cyclobutadiene (1), chemists have been seeking ways of diminishing its high reactivity and increasing its stability. One way has been by complexation with a transition metal moiety, thereby "freezing" the cyclobutadiene into relative inertness. Examples of such complexes include cyclobutadieneiron tricarboxyl (2),\(^5\) benzocyclobutadieneiron tricarboxyl (3),\(^5\) tetrphenylcyclobutadieneiron tricarboxyl (4),\(^6\) tetrphenylcyclobutadienepalladium chloride (5),\(^7\) tetrphenylcyclobutadieneneickel bromide (6),\(^8\) and tetramethycyclobutadieneneickel bromide (7).\(^9,10\)

\[\text{[Chemical Structures]}\]

Stability can also be attained by fusion to aromatic rings. Stabilization in this way can be attributed to the decrease in \( \pi \)-bond order in the four-membered ring system, thus making it less cyclobuta-
dienoid and more quinonoid in character. An example of this kind of stabilization was first observed by Lothrop\(^{\text{11}}\) who reported the syn-

\[ \text{(8a)} \quad \text{(8b)} \quad \text{(8c)} \]

\[ \text{(9)} \quad \text{(8e)} \quad \text{(8d)} \]

\[ \text{(10)} \quad \text{(11)} \quad \text{(12)} \]

\[ \text{(13)} \quad \text{(14)} \quad \text{(15)} \quad \text{(16)} \]

thesis of biphenylene (8) in 1941. Thus, as shown by Mak and Trotter, of the five possible canonical resonance forms of 8, 8d and 8e would be expected to be the least important contributors to the resonance hybrid. Interesting benzo derivatives of biphenylene (8) include benzo[\(c\)]biphenylene (9),\(^{13}\) dibenzo[\(b, h\)]biphenylene (10),\(^{14}\) benzo[\(a\)]biphenylene (11),\(^{14}\) dibenzo[\(a, j\)]biphenylene (12),\(^{15}\) dibenzo[\(a, g\)]biphenylene (13),\(^{16}\) and the newly synthesized dibenzo[\(a, g\)]biphenylene (14).\(^{17}\) From theoretical studies it has been concluded that linearly annellated benzobiphenylenes should be more stable than biphenylene itself and that angularly annellated benzobiphenylenes should be less stable than biphenylene. Thus, it has been established experimentally that although 8, 9, and 10 are stable at their melting points, 12, 13, and 14 are not; that solutions of 11, 12, 13, and 14 are destroyed on exposure to ultraviolet light, whereas 8, 9, and 10 are not; and that 14 (which bears an interesting structural resemblance to the hypothetical 1,2-diphenylbenzocyclobutadiene (15) which will be referred to later) adds bromine to give the dibromide (16), which on treatment with sodium iodide reverts back to 14.\(^{17}\)

With the knowledge that stabilization of the cyclobutadiene system


can be effected by fusion on both sides to aromatic rings, it becomes of interest to try to design and synthesize cyclobutadienes fused on only one side to an aromatic ring. The simplest such molecule is benzo-cyclobutadiene (17). In 1952, Roberts and coworkers\(^1\) predicted on the basis of molecular orbital theory that 17 should have a singlet electronic ground state and that it should possess substantial delocalization energy (about 48 kcal/mole). Of the three canonical resonance forms that can be written, 17c should be the least important contributor to the hybrid because of the high energy quinonoid system. The most important contributor should be 17a because it is not cyclobutadienoid. This is in agreement with the bond orders calculated for 17 by molecular orbital theory.

\[
\begin{align*}
\text{(17a)} & \quad \leftrightarrow \quad \text{(17b)} & \quad \leftrightarrow \quad \text{(17c)}
\end{align*}
\]

A few years after Roberts' calculations, after discovering an interesting set of reactions recorded in a dissertation by Finkelstein,\(^1\) then a student of Thiele, Cava\(^2\) reported his reinvestigation of these reactions, the results of which led to the conclusion that benzo-cyclobutadiene (17) had been generated as an unstable transient intermediate. When \(a, a', a'' - t\)-trabromo-\(o\)-xylene (18) was treated with sodium iodide in ethanol, 1,2-dibromobenzo-cyclobutene

\[18 \text{ H. Finkelstein, Ph. D. dissertation, University of Strasbourg (1909).}
\]

(19) was formed. Treatment of 19 with zinc in ethanol led to the dihydrobenzobiphenylene (20). Compound 20 was then postulated to arise from a dimerization via a Diels-Alder reaction of 17. Benzocyclobutadiene (17) was also generated by the reaction of 1-bromobenzocyclobutene (21) with potassium t-butoxide.\(^{20}\) Conclusive evidence for the existence of 17 was given by trapping it with active dienes and dienophiles to give the corresponding Diels-Alder adducts.\(^{21,22}\)

\[
\begin{align*}
\text{(18)} & \quad \begin{array}{c}
\text{CHBr}_2 \\
\text{CHBr}_2 \\
\text{NaI} \\
\text{(19)} \\
\text{(17)} \\
\text{Br} \\
\text{Br} \\
\text{t-BuOK} \\
\text{(21)} \\
\end{array} \\
\end{align*}
\]

Other modes of dimerization of 17 have been observed. When the dibromide (19) was dehalogenated in the presence of nickel tetracarbonyl, a linear dimer (22), in contrast to the angular dimer (20), was

\(^{20}\text{Ibid., 80, 2255 (1958).}\)


formed. More recently, a new dimer of 17 has been reported. When benzocyclobutadieneiron tricarbonyl (3) was treated with silver nitrate, 17 was generated and the dimer (25) was isolated.

Unstable benzocyclobutadiene derivatives with halogen substituents in the 1- and 2-positions have also been generated and isolated as their dimers or trapped with active dienes. Roberts had predicted that phenyl substituents in the 1- and 2-positions should contribute much to the stability of the benzocyclobutadiene system. A number of attempts have been made along this line with the result that (a) the

---


synthesis of 1,2-diphenylbenzocyclobutadiene (15) as attempted by Coleman was unsuccessful because certain of its precursors did not undergo the expected reactions and led to useless products; (b) the benzo-cyclobutadienes (24) and (26) as generated by Stiles via the intermediate benzylene were unstable intermediates and were isolated only as the dimeric cyclooctatetraenes (25) and (27); or (c) the generation of 26 as performed by Blomquist was in doubt.

\[
\begin{align*}
\text{H}_3\text{O}^+ \quad \text{C}_2\text{H}_5=\text{C}-\phi \\
\text{H}_3\text{O}^+ \quad \text{C}_2\text{H}_5=\text{C}-\phi
\end{align*}
\]


Because of the interesting chemistry that benzocyclobutadiene (17) and its derivatives exhibit, the question arises as to what effect fusing additional benzene rings to the benzene nucleus in 17 will have on the system's stability. From molecular orbital calculations on naphtho[al]cyclobutadiene (28), naphtho[ll]cyclobutadiene (29), and phenanthro[ll]cyclobutadiene (30) it was found that 28 and 30 should be less stable than benzocyclobutadiene (17) and 29 should be more stable.28,29

29 H. S. Lee, Chemistry (Taipei), 1963, 22.
Experimeotally, thi s seems to be the case. Thus, although Nenitze- 
sucu\textsuperscript{30,31} succeeded in generating 3,8-diphenylnaptho\[2\]
cyclobutadiene (31) and found it to be unstable, Cava's group synthesized 1,2-diphen- 
ylnaphtho\[2\] cyclobutadiene (32)\textsuperscript{32} and 1,2-dibromo-3,8-diphenylnaptho- 
\[2\] cyclobutadiene (33)\textsuperscript{33} and found them to be stable compounds. Both 
of these compounds, (32) and (33), were the first two stable cyclo- 
butadiene derivatives ever to be reported which were not fused on 
both sides to aromatic rings or complexed with transition metals. 
Cava\textsuperscript{33} also reported the generation of 1-bromo-3,8-diphenylnaptho- 
\[2\] cyclobutadiene (34) which proved to be unstable and was trapped as 
the Diels-Alder adduct (36) with 1,3-diphenylisobenzofuran (35). It 
appears that one bromine atom on the four-membered ring does not 
sufficiently stabilize the system to allow its isolation, whereas 
the addition of a second bromine atom is sufficient.

Cava\textsuperscript{34} has also reported the generation of 1,2-diphenylphenan- 
 thro\[3\] cyclobutadiene (38) by treatment of the dibromide (37) with 
zinc or nickel tetracarbonyl. It was found that the cyclobutadiene 
(38) was unstable and led to polymer or in the presence of air gave

\footnotesize{
\textsuperscript{30} O. D. Nenitzescu, M. Avram, I. G. Dimulescu, and G. Mateescu, 

\textsuperscript{31} M. Avram, I. G. Dimulescu, M. Elian, M. Farcasiu, E. Marica, 

\textsuperscript{32} M. P. Cava, B. Y. Hwang, and J. P. Van Meter, J. Am. Chem. 

\textsuperscript{33} M. P. Cava and B. Y. Hwang, Tetrahedron Letters, No. 27, 
2297 (1965).

\textsuperscript{34} M. P. Cava and D. Mangold, Tetrahedron Letters, No. 26, 1751 
(1964).
}
9,10-dibenzoylphenanthrene (39) in 85% yield. The fact that 1,2-diphenyl-naphtho[12]cyclobutadiene (32) is stable and the phenanthro[12]cyclobutadiene (38) is unstable substantiates the prediction made earlier from molecular orbital theory as to their relative stabilities.28,29

Evidence for the existence of a stable derivative of cyclobutadiene which is not fused to an aromatic ring or in the form of a transition metal complex has been described by Cookson and coworkers in which they generated tetraphenylocyclobutadiene (40) in two ways.35,36 The first method was by treating tetraphenylocyclobuta- 


dienespalladium chloride (5) in the absence of air with triphenylphosphine in benzene or chloroform to give green solutions. After allowing to stand, the dimeric product octaphenylcyclooctatetraene (41) was isolated. When the solutions were exposed to air, the color faded instantly and tetraphenylfuran (42) was obtained. When 40 was generated in the presence of methyl phenylacetylene carboxylate (43), methyl pentaphenyldisazoate (44) was isolated. The other method by which 40 was generated was by heating the complex (5) to 185° in vacuo to give a volatile material, a mass spectrum of which gave strong support for the existence of 40 in the gas phase.
II. STATEMENT OF PROBLEM

The prime objective of this work was to synthesize a stable derivative of benzocyclobutadiene (17). In particular, since it has been predicted that phenyl substituents in the 1- and 2-positions should add considerable stabilization to the system, \textsuperscript{1} 1,2-diphenylbenzocyclobutadiene (15) would have been an appropriate choice. However, the synthesis of 15 had been attempted earlier without success. One method involved trying to induce benzyne to react with diphenylacetylene, but no reaction was observed to take place between the two.\textsuperscript{26} The more classical and straightforward method was to halogenate 1,2-diphenylbenzocyclobutene (45) and dehalogenate the resulting dihalide (46) with zinc or sodium iodide. In fact, when halogenation of 45 was attempted with bromine, N-bromosuccinimide, or sulfuryl chloride, only tar, 9-phenylanthracene (47), or 9-chloro-9,10-dihydro-10-phenylanthracene (48), respectively, could be isolated.\textsuperscript{25} The most probable explanation for these undesired transformations is that, as shown in Chart I (page 15), the cyclobutene ring in 45 is easily opened thermally to give the nicely stabilized singlet diradical (49) or the o-quinodimethane (50). The open intermediate can then either cyclize to 9,10-dihydro-9-phenylanthracene (51) which can then be halogenated and lose hydrogen halide to give 47, or it can add a halogen atom and then cyclize to the anthracene system. The latter pathway appears to be the more favorable one under
CHART I

The Halogenation of 1,2-Diphenylbenzocyclobutene

\[ X = \text{Cl or Br} \] (46)

\[ (45) \]

\[ \xrightarrow{\text{Brs}} \text{tar} \]

\[ (47) \]

\[ \xrightarrow{\text{SO}_2\text{Cl}_2} \]

\[ (48) \]

\[ (45) \xrightarrow{\Delta} \]

\[ (49) \leftrightarrow (50) \]

\[ (51) \]

\[ \xrightarrow{X^*} \]

\[ \xrightarrow{\text{(-HX)}} \]

\[ (47) \]
these conditions in the light of Carpino's work, whereby cis-1,2-diphenylbenzocyclobutene (45a) was transformed into trans-1,2-diphenylbenzocyclobutene (45b) in refluxing carbon tetrachloride and no mention of the presence of 51 in the product was made.  

\[
\begin{align*}
\text{(45a)} & \quad \xrightarrow{\text{\phi}} \quad \begin{array}{c}
\frac{\hphantom{0}}{(49)} \swarrow \searrow \nearrow \nwarrow \\
\frac{\hphantom{0}}{(50)} \quad \xrightarrow{\text{\phi}} \quad \text{(45b)}
\end{array}
\end{align*}
\]

On the other hand, Cava\(^{34}\) discovered that bromination of trans-1,2-diphenylphenanthro[1,1]cyclobutene (52) with N-bromosuccinimide proceeds to give 1,2-dibromo-1,2-diphenylphenanthro[1,1]cyclobutene (57). This is in contrast to what would have been predicted on the basis of strain and electronic effects. Because the \(\pi\) bond in phenanthro[1,1]cyclobutene (53a)\(^*\) at the juncture of the four- and six-membered rings is of higher order than that in benzocyclobutene (54a), the four-membered ring in 53a should possess more strain and therefore have a greater tendency to open. Also, in comparing the open forms (53b) and (54b) of 53a and 54a, respectively, the amount of o-quinonoid character should be less in 53b because of the lower


\(^*\) Recently, two concurrent communications appeared, one by Masamune and Kato and one by White and coworkers, in which mention is made of 53a as being the probable corrected structure of the previously erroneously assigned diphenyltetrahe drane. See refs. 38 and 39.


π-bond order at the two six, six ring junctures than of the corresponding bonds on 54b, and this also should give 53a a greater tendency to open. The only explanation to account for the contradictory
result is that of the buttressing effects of the hydrogens at C-3 and C-10 on the phenyl substituents. In the open form of 52 there is heavy steric interaction between the 3- and 10-hydrogens and the phenyl groups causing the latter to be twisted out of planarity with the phenanthrene system. This decreases the degree of conjugation in the system thus lowering the amount of resonance stabilization. Also arising from this steric interaction is a compression effect exerted by the 3- and 10-hydrogens which tend to keep the four-membered ring closed.

Because of this finding, it was felt that if the proper substituents were chosen and put in the 3- and 6-positions of 1,2-diphenylbenzocyclobutene (45) to give 55, the thermal ring opening tendency would be discouraged and halogenation should proceed in the desired manner to give the 1,2-dihalide (56) which could then be dehalogenated to give the 1,2-diphenylcyclobutadiene (57). Certain restrictions as to the nature of the 3- and 6-substituents had to be imposed before choosing them: (a) they had to be spherically symmetrical so that steric interaction with the 1- and 2-phenyl substituents would not be minimized by the former twisting into a more favorable conformation; (b) they had to be about the same size as a methyl group so as to exert a steric effect near to that exerted by the 3- and 10-hydrogens in 52; (c) they had to be rather chemically inert, especially toward halogenation; (d) they had to have as little electronic influence as possible on the benzocyclobutadiene system so that the cyclobutadiene (57) would electronically resemble 1,2-diphenylbenzo- cyclobutadiene (45) as closely as possible. From these considerations
it was felt that bromine atoms would fit quite nicely the properties required of the benzene ring substituents. The compound thus chosen as the ultimate goal of synthesis was 1,2-diphenyl-3,4,5,6-tetrabromo-benzocyclobutadiene (58). The reason for four bromine atoms on the benzene ring was because of the much more ready availability of the potential starting materials.

Three possible approaches to the synthesis of 1,2-diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59) were proposed. One was to prepare 1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60), which could then be halogenated to the corresponding α,α'-dihalide (61), as was reported to be performed on α-dibenzylbenzene (65) by Baker and McOmie. Treatment of 61 with sodium iodide in the manner of Coleman could then give the desired cyclobutene (59). An alternative approach was to synthesize 1-benzyl-2-(α-hydroxybenzyl)-3,4,5,6-

---

tetraphthalobenzene (64) which, by analogy with Van Meter's procedure used in the synthesis of trans-1,2-diphenylnaphtho b cyclobutene (68), could be converted to the corresponding α-chloro derivative (65) and induced to eliminate hydrogen chloride under the influence of base to give 59. The third approach consisted of converting the α,α'-dihalide (61) to the cyclic thioether (66) with sodium sulfide or, alternatively, synthesizing the α,α'-dihydroxy

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42 This procedure was an adaptation of that used in the synthesis of trans-1,2-diphenylbenzocyclobutene (45b) which was developed by Dr. A. J. Berlin who transmitted the details to Prof. M. F. Cava by direct communication.
derivative (62) which could be converted to 66 with phosphorus pentasulfide. Oxidation of 66 could lead to the sulfone (67) which could give the desired 59 by photolytic expulsion of sulfur dioxide.
III. DISCUSSION AND INTERPRETATION OF RESULTS

At the outset of this work no serious obstacles were anticipated along the synthetic path to 1,2-diphenyl-3,4,5,6-tetrabromo-benzocyclobutene (59). This was expected because certain reactions to be used in the proposed synthetic schemes had analogies in the unbrominated series, and the other reactions were considered to be straightforward and classical. The major difficulties were expected to arise in the conversion of 59 to 1,2-diphenyl-3,4,5,6-tetrabromo-benzocyclobutadiene (58). As it happened, however, all attempts in this work to prepare 59 failed. The inability of some compounds to react or their tendency to undergo undesirable reactions was attributed to the effects produced by the four bromine substituents. They either were displaced by other attacking reagents, prevented reactions from taking place by imposing steric hindrance, or induced unexpected reactions to take place by virtue of the compression effect they exerted on the ortho carbon functions. The following discussion is a description of the observations and results obtained during the attempts made in this work to synthesize the benzocyclobutene (59) and certain of its possible precursors.

In order to synthesize 1,2-diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59), possible synthetic routes were envisaged which made use of three readily available starting materials: tetrabromophthalic anhydride (69), a commercially available material being
marketed chiefly for use as a fire retardant; 3,4,5,6-tetrabromo-o-xylene (70), a known compound easily synthesized from o-xylene; and 3,4,5,6-tetrabromo-o-toluic acid (71), an unknown compound derivable from o-toluic acid.

The first approach at the synthesis of 59 began with tetra-bromophthalic anhydride (69). A Friedel-Crafts reaction of 69 with benzene in the presence of anhydrous aluminum chloride afforded the known hydroxy lactone, 3-hydroxy-3-phenyl-4,5,6,7-tetrabromophthalide (72), although it was reported as the keto acid, 2-benzoyl-3,4,5,6-tetrabromobenzoic acid (73). Here was encountered the first example in this work of the compression effect on the two ortho substituents (here, benzoyl and carboxyl) exerted by the flanking bromine atoms. This effect has been observed in derivatives of o-benzoylbenzoic acid where methyl groups were in the positions ortho to the benzoyl and carboxyl groups. Apparently, the keto acid form (73) is not capable of existing. The carbonyl infrared absorption provided conclusive evidence that the Friedel-Crafts product was 72 and not the open acid (73) by the fact that there was

43 A. Hofmann, Monatsh., 36, 805 (1915).
only one carbonyl absorption at 5.7 μ which indicated a phthalide-type carbonyl.

\[ (69) \xrightarrow{\text{O} \text{HBr}} \text{Br} \]

(72)

\[ \text{Br} \]

\[ \text{Br} \]

\[ \text{Br} \]

\[ \text{Br} \]

\[ \text{Br} \]

\[ \text{OH} \]

\[ \text{Br} \]

\[ \text{Br} \]

\[ \text{CO}_2\text{H} \]

(73)

With one phenyl substituent in place, the next objective was to put a second phenyl group on the other carbon function. In order to effect this conversion, the plan was to reduce 72 to 2-benzyl-3,4,5,6-tetabromobenzoic acid (74), transform 74 to its acid chloride (75), and by either direct Friedel-Crafts reaction with benzene, or conversion of 75 to the nitrile (76) and reaction with phenyl-magnesium bromide would give 1-benzyl-2-benzyl-3,4,5,6-tetabromobenzene (77).

\[ \text{Br} \]

\[ \text{Br} \]

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

\[ \text{Br} \]

\[ \text{Br} \]

\[ X \]

(74): \( X=\text{CO}_2\text{H} \)

(75): \( X=\text{COCl} \)

(76): \( X=\text{CN} \)

\[ \text{Br} \]

\[ \text{Br} \]

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

\[ \text{Br} \]

\[ \text{Br} \]

\[ \phi \]

(77)

When catalytic hydrogenation of 72 was attempted, only starting material was recovered. The apparent inertness of the molecule under these conditions may be attributed to the absence of a benzophenone-type carbonyl which should ordinarily be reduced to a methylene group. Because the sodium salt of 72 existed in the open form as
sodium 2-benzoyl-3,4,5,6-tetrabromobenzoate (78), as the infrared carbonyl absorptions at 6.0 μ and 6.2-6.3 μ corresponding to the ketone carbonyl and carboxylate carbonyl, respectively, showed, catalytic reduction was tried. Indeed, the ketone carbonyl was reduced as expected, but not expected was the total reductive dehalogenation of the molecule to give as the isolated product α-benzylbenzoic acid (79), identical in all respects with authentic 79. Such reductive dehalogenations using nickel or palladium catalysts in the presence of alkali have been known for some time and have been useful in displacing halogen substituents by hydrogen.  

Because it was known that catalytic hydrogenation of 3-phenylphthalide (80) gave α-benzylbenzoic acid (79) quantitatively, it was hoped that the analogous transformation would occur with 3-phenyl-4,5,6,7-tetrabromophthalide (81). The phthalide (81) was prepared from the hydroxy lactone (72) according to Newman’s procedure for converting α-benzoylbenzoic acid (82) to 3-phenylphthalide


whereby the sodium salt of the acid was treated with sodium borohydride for several days. Isolation of the hitherto unknown phthalide (81), m.p. 251-255°, was accomplished. The infrared spectrum showed a strong band at 5.7 μ indicative of a phthalide carbonyl, and there was no hydroxyl absorption. Attempted catalytic hydrogenation of 81, however, gave only starting material.

It was later found that 81 could be prepared in another way from the hydroxy lactone (72) by conversion of the latter with thionyl chloride to 3-chloro-3-phenyl-4,5,6,7-tetrabromophthalide (83), which on catalytic hydrogenation gave 81. The chloro lactone (83), m.p. 248-250°, did not appear to hydrolyze on standing for months in the air. Its infrared spectrum showed a carbonyl absorption at 5.6 μ and no hydroxyl absorption.

Reduction of 81 using zinc in acetic acid in the presence of

hydrochloric acid gave a white crystalline product, \( \text{C}_{14}\text{H}_8\text{Br}_8\text{O}_2 \), m.p. 184-185.5\(^\circ\), which gave an infrared spectrum possessing a carbonyl absorption at 5.7 \( \mu \) and no hydroxyl absorption indicating the phthalide structure was still present. From these data it appears that the desired reduction did not take place, but rather, reductive dehalogenation of two bromine atoms took place to give a dibromo-phthalide \((84)\). No further structure elucidation was attempted in order to determine the positions of the remaining bromine atoms, but it might be supposed that if the ones at the more activated positions — that is, ortho and para to the carbonyl — were displaced by hydrogen, the product should be 4,6-dibromo-3-phenylphthalide \((85)\).

\[
(\text{81}) \xrightarrow{\text{Zn, HOAc (HCl)}} \begin{array}{c}
\text{Br} \\
\text{H} \\
\text{Br}
\end{array}
\]

\[
\text{(84)}
\]

\[
(\text{85})
\]

Treatment of 3-phenyl-phthalide \((80)\) with phenylmagnesium bromide and subsequent acidification was known to give 1,3-diphenyliso-benzofuran \((35)\) which could be easily oxidized to \( \alpha \)-dibenzoylbenzene \((86)\).\(^47\) Thus, the tetrabromophthalide \((81)\) was treated with phenylmagnesium bromide under a variety of conditions, but either starting material was recovered or uncrystallizable oils were obtained, and the reaction was not pursued any further. Similarly, it had been known that the reaction of 3-chloro-3-phenylphthalide \((87)\) with phenylmagnesium bromide gave 86 directly.\(^48\) When this reaction was

tried with the 3-chlorotetabromophthalide (83), either starting material or oils were obtained, depending upon the conditions employed, and like before, this reaction was abandoned. In both reactions a two- to threefold excess of phenylmagnesium bromide was required and the reaction mixture had to be heated before all of the starting material would disappear. From this result it appears that initial attack on the carbonyl by phenylmagnesium bromide is substantially hindered by the neighboring bromine atom and that coupling with the benzene ring by displacement of bromide is significantly competitive if not preferred.

As a final attempt in this series at putting the second phenyl group on the phenyl-free carbon function, 3-chloro-3-phenyl-4,5,6,7-tetabromophthalide (83) was subjected to a Friedel-Crafts reaction with benzene in the presence of aluminum chloride in hopes of obtaining 1,2-dibenzoyl-3,4,5,6-tetabromobenzene (88). The white
crystalline product, m.p. 279-281°, had an infrared carbonyl absorption at 5.7 μ indicative of a phthalide structure. On this basis, the product was assigned the structure of 3,3-diphenyl-4,5,6,7-tetramethoxyphthalide (89). Indeed, the analogous reaction with the chloro lactone (87) has been reported to give 3,3-diphenylphthalide (90).

\[
\text{Br O} \quad \text{Br} \quad \text{Br} \\
\text{Br} \quad \text{Br} \quad \text{O} \\
\text{Br} \quad \text{Br} \quad \text{O}
\]

At this point it appeared that the series of compounds derived from tetrabromophthalic anhydride (69) would not allow a simple entry into the particular group of compounds which could serve as possible precursors to 1,2-diphenyl-3,4,5,6-tetramethoxybenzocyclobutene (59). It was therefore decided to go back and begin a fresh approach. The starting material chosen for this new approach was 3,4,5,6-tetramethoxy-o-xylene (70), the preparation of which had first been reported in 1884, whereby o-xylene was converted into 70 by the action of bromine in sulfuric acid. In this work a slight modifi-

50 P. O. Blümlein, Ber., 17, 2485 (1884).
cation of a more recent and convenient preparation was used in which 
\( \alpha \)-xylene was brominated in the presence of iron powder. 51

It has recently been reported that Friedel-Crafts alkylation of 
benzene with \( \alpha, \alpha', \alpha'', \alpha''' \)-tetrachlorodurene (91) at 8-10\(^{\circ}\) in the 
presence of anhydrous ferric chloride gives 1,2,4,5-tetra 
benzylbenzene (92) in 52\% yield. 52 Therefore, reaction of 70 with bromine 
in the presence of light in refluxing carbon tetrachloride gave the 
unknown \( \alpha, \alpha', 3,4,5,6 \)-hexabromo-\( \alpha \)-xylene (93), m.p. 166-167.5\(^{\circ}\). When 
93 was analogously subjected to a Friedel-Crafts reaction under the 
same conditions used in the preparation of 92, no apparent reaction 
took place. However, upon refluxing the reaction mixture, the reaction proceeded as anticipated and afforded 72\% of 1,2-dibenzyl-
3,4,5,6-tetrabromobenzene (60), which in the pure state melted at 
219-221\(^{\circ}\). There are two possible reasons which can be given to ac-
count for the fact that higher temperatures were required in the 
reaction involving 93 than that involving 91. One is that the steric 
bulk of the bromines flanking the bromomethyl groups makes it more 
difficult for benzene to attack the intermediate benzyl carbonium ion.
A second possible explanation is that the four ring bromine sub-
stituents cause destabilization of the intermediate benzyl carbonium 
ion by virtue of the fact that they are highly electronegative and 
therefore inductively electron withdrawing, thereby making the forma-
tion of the carbonium ion more difficult. If either or both explana-

424 (1946).

tions are true, the stability of 1,2-diphenyl-3,4,5,6-tetrabromobenzo-
butadiene (58), if it were ever synthesized, might actually be greater
than that of 1,2-diphenylbenzocyclobutadiene (15) itself. For one,
the bromine atoms flanking the four-membered ring might sterically
help in protecting the 1- and 2-positions from attack by certain re-
agents. Also, the inductive electron withdrawing effect of the
bromine substituents could help decrease the electron density in the
cyclobutadiene system thereby making it more stable.

Now that a compound with a phenyl substituent on each of the
two α-positions of the α-xylene system had been secured, it remained
only to functionalize either one or both of the methylene carbons in
order that closure to a four-membered ring might subsequently be
performed. One way to effect such functionalization might be to
halogenate the methylene carbons, as was done by Baker and McOmie
who allowed α-dibenzylbenzene (65) to react with either one or two
equivalents of N-bromosuccinimide to obtain α-bromo-α-dibenzylbenzene
(94) or α,α'-dibromo-α-dibenzylbenzene (95), respectively. When
1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60) reacted with one equivalent of N-bromosuccinimide and the product immediately treated with potassium t-butoxide, all that could be isolated was the starting material in over 60% yield. Here, according to the procedures of Van Meter and Berlin, the intermediate \( \alpha,3,4,5,6 \)-pentabromo-1,2-dibenzylbenzene (96), if formed, should have reacted with the potassium t-butoxide to give 1,2-diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59).

When slightly more than 2.5 equivalents of N-bromosuccinimide were used, all that was isolated was a yellow crystalline compound, \( \text{C}_{20}\text{H}_{10}\text{Br}_4 \), m.p. 222-223°. Its nuclear magnetic resonance spectrum showed peaks in the aromatic region only centering at about 7.4 δ. It did not react with bromine or potassium permanganate, as it might have been expected to do if it were the benzocyclobutadiene (58). Its ultraviolet spectrum was very similar to that of 9-phenylanthracene (47), the major difference being that the absorptions of the bromination product of 60 were shifted to longer wavelengths than those of 47. When the compound was reductively dehalogenated by catalytic hydrogenation in the presence of triethylamine, 9-phenylanthracene (47) was isolated. Furthermore, the same yellow bromination product was obtained when 9,10-dihydro-9-phenyl-1,2,3,4-tetra-bromoanthracene (97), a compound which was later secured and which
will be discussed in more detail later, reacted with N-bromosuccinimide. On the basis of these data the yellow bromination product of 60 was assigned the structure of 9-phenyl-1,2,3,4-tetraphthalocyanine (98). The same product (98) was obtained when halogenation was attempted with bromine or sulfuryl chloride.

This particular rearrangement was not surprising since 94 and 95 had been reported to rearrange and cyclize to form six-membered rings to give the anthracene derivatives 47 and/or 51 depending on the conditions used. In the case at hand, as indicated in Chart II (page 34), the initial benzhydryl radical formed can do one of two things: (a) it can attack the phenyl ring of the ortho benzyl group directly to give the intermediate 9,10-dihydro-9-phenyl-1,2,3,4-tetraphthalocyanine (97), or (b) it can halogenate to give the a-halo derivative (96), the dissociation of which should give a fairly stable benzhydryl carbonium ion which can then perform an electrophilic attack on the phenyl of the ortho benzyl group to give 97. Halogenation of 97 followed by dehydrohalogenation should then give the anthracene (98). Because the latter mechanistic pathway was believed to be the more favorable one, it was reasoned that if a powerful electron withdrawing group could be put on each of the two phenyl rings of the benzyl groups, the phenyls might be sufficiently deactivated toward electrophilic substitution that attack by the intermediate benzhydryl carbonium ion to form a six-membered ring might not take place.

In the first attempt made along these lines, nitration of the phenyl groups was tried, but pure products could not be obtained.
The Halogenation of 1,2-Dibenzyl-3,4,5,6-tetramethoxybenzene (60)

\[
\begin{align*}
(60) & \\
(59) & \\
(97) & \\
(96) & \\
(98) & \\
(47) & 
\end{align*}
\]
Reaction of 60 with benzenesulfonyl chloride in the presence of aluminum chloride gave the expected 1,2-bis(p-benzenesulfonylbenzyl)-3,4,5,6-tetrabromobenzene (99) as white crystals which had two melting points: one at 140° when it became semicrystalline but was fully crystalline again by 165°, and another at 269-270°. As a check that the first melting point did not represent a permanent alteration in the molecular structure of the compound, a sample was melted, cooled, and recrystallized from chloroform. Its infrared spectrum was identical to that of the unmelted material.

When 99 reacted with bromine under the influence of light, the product isolated was obtained as greenish yellow needles, m.p. 252-253.5°, whose analysis was consistent with the formula C_{36}H_{18}Br_{4}O_{4}S_{2}. A strong similarity was observed between the ultraviolet spectrum of the bromination product and that of 9-phenyl-1,2,3,4-tetrabromoanthracene (98). As a check, the effect of the benzenesulfonyl groups on the ultraviolet spectrum was determined by comparing the ultraviolet spectra of 1,2-bis(p-benzenesulfonylbenzyl)-3,4,5,6-tetrabromobenzene (99) and 1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60). The spectra of 99 and 60 were very similar, the major difference being a bathochromic shift of most of the absorptions of 99 over those of 60. The spectrum of the bromination product of 99 bore a similar relationship to the spectrum of 98 in that the major difference in the two spectra lies in the fact that most of the absorptions of the bromination product were shifted to longer wavelengths over those of 98. From these data and mechanistic considerations, the compound obtained on bromination was designated to
be 7-benzenesulfonyl-9-(p-benzenesulfonylphenyl)-1,2,3,4-tetrabromoanthracene (100).

This surprising result is indicative of the nature of the process taking place during bromination of the o-dibenzylbenzene derivatives (60) and (99). First, as pointed out before, the intermediate benzhydryl radical could be attacking the opposite phenyl ring, in which case a deactivating substituent on that ring should not have much influence on the attacking ability of the radical, especially since it is all set up sterically to do so. Second, if it is the benzhydryl carbonium ion which is attacking, this is a demonstration of the powerful steric effect which the flanking bromine atoms have on compressing the two benzyl groups together. The carbonium ion is
forced into alkylation a benzene ring, admittedly at a position _meta_
to a benzenesulfonyl group, but, which is, nevertheless, highly de-
activated.

It was found that the benzenesulfonyl derivative (99) formed
deep purple solutions in N,N-dimethylformamide or dimethylsulfoxide
with strong bases, indicating that it was forming an anion. It was
decided to try to take advantage of this and functionalize the
methylenecarbons _via_ the anion. Thus, 99 was dissolved in N,N-
dimethylformamide and treated with potassium t-butoxide followed by
n-butyl nitrite. No oximated product was formed, however, and all
that could be isolated was starting material. Attempted oxidations
of the anion under a variety of conditions gave either starting mate-
rial or intractable oils.

As a last resort in the dibenzyl series, direct chromic acid
oxidation of 60 was tried in order to effect conversion of the methy-
lene groups to carbonyl groups. Several attempts were made, but here
again, no crystalline products other than starting material could be
isolated.

At this point it was again decided that a fresh approach was
necessary and that a new starting material should be looked for. In
the earlier two attempts, the starting material in each case had both
of the _ortho_ carbon functions in the same oxidation level. The plan
in this third approach was to find a starting compound in which the
ortho carbon functions were not in the same oxidation level. The
molecule thus chosen was the hitherto unreported 3,4,5,6-tetrabromo-
α-toluic acid (71), m.p. 236.5-237.5°. This compound was easily pre-
pared by the reaction of \( \sigma \)-toluic acid with bromine in the presence of anhydrous aluminum chloride. As indicated in Chart III (page 39), the reaction of 71 with thionyl chloride gave the expected acid chloride (101), m.p. 128.5-130.5\(^\circ\), a stable compound which could be kept for months without any apparent decomposition. A Friedel-Crafts reaction of 101 with benzene in the presence of aluminum chloride gave 2-benzoyl-3,4,5,6-tetramethylbenzene (102), m.p. 162-163.5\(^\circ\), whose infrared spectrum showed a carbonyl absorption at 6.0 \( \mu \), indicative of a benzophenone carbonyl. Reaction of 102 with bromine in the presence of light gave 2-benzoyl-3,4,5,6-pentabromotoluene (103), m.p. 143.5-145\(^\circ\). This was permitted to react with benzene in the presence of aluminum chloride to give 1-benzoyl-2-benzyl-3,4,5,6-tetramethylbenzene (77), m.p. 155-156\(^\circ\), which was obtained in the crude state (m.p. 135-150\(^\circ\)) in an overall yield of 43% from the starting material \( \sigma \)-toluic acid. The infrared spectrum of 77 showed a carbonyl absorption at 6.0 \( \mu \), and its nuclear magnetic resonance spectrum showed a singlet at 4.10 \( \delta \) (methylene protons) and a broad multiplet centering at 7.4 \( \delta \) (aromatic protons) in the ratio of 2:10.

At this point, the first major objective had been reached: to secure a derivative of 1,2-dibenzyl-3,4,5,6-tetramethylbenzene (60) where one or both of the methylene carbons has been functionalized. From here, there were two foreseeable pathways open into the generation of the four-membered ring. One was to reduce the carbonyl in 77 to an hydroxyl group and by means of Van Meter's procedure, as described before, convert the alcohol (64) to the benzocyclobutene
CHART III

The Synthesis of 1-Benzyl-2-(α-hydroxybenzyl)-3,4,5,6-tetrabromobenzene (64) from 2-Toluic Acid

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{COOH} & \xrightarrow{\text{Br}_2, \text{AlCl}_3} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} \\
\text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} & \xrightarrow{\text{Br}_2, \text{AlCl}_3} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} \\
\text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} & \xrightarrow{\text{C}_{6}\text{H}_6, \text{AlCl}_3} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} \\
\text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} & \xrightarrow{\text{C}_{6}\text{H}_6, \text{AlCl}_3} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} \\
\text{C}_{6}\text{H}_{4}\text{CH}_2\text{COOH} & \xrightarrow{\text{LiAlH}_4} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{OH} \\
\text{C}_{6}\text{H}_{4}\text{CH}_2\text{OH} & \xrightarrow{\text{LiAlH}_4} \text{C}_{6}\text{H}_{4}\text{CH}_2\text{OH} \\
\end{align*}
\]
The other possible approach was to transform the methylene group into another carbonyl group to give 1,2-dibenzoyl-3,4,5,6-tetrabromobenzene (88) which could be reduced to the diol (62) and, as also described earlier, could be converted into 59.

![Structure](image)

(88)

The ketone (59) failed to react with sodium borohydride, but reduction with lithium aluminum hydride did occur to give the desired product, 1-benzyl-2-(a-hydroxybenzyl)-3,4,5,6-tetrabromobenzene (64). Van Meter's procedure was tried by treating the alcohol (64) with thionyl chloride at an initial temperature of about -15° and allowing the mixture to warm to room temperature followed by removal of the excess thionyl chloride. The remaining material was refluxed with potassium t-butoxide. Aside from starting alcohol (64), a compound, C_{13}H_{16}Br_{4}, was isolated which melted at 75.5-77° and gave a nuclear magnetic resonance spectrum showing a singlet at 4.13 δ and a multiplet centering at 7.3 δ in the ratio of 1:3. These data were incompatible with the structure of the expected 1,2-diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59). On closer study of the product mixture, benzoic acid was discovered. When the alcohol (64) was refluxed with potassium t-butoxide, followed by addition of water and refluxing a little while longer, the same compound as isolated before was obtained along with benzoic acid. On the basis of the
information gathered, the compound was assigned the structure of 2,3,4,5-tetrabromodiphenylmethane (104).

\[
\begin{align*}
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Cl} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{OH} & \quad \text{Br} & \quad \text{OH} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{CH} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{OH} & \quad \text{Br} & \quad \text{OH} & \quad \text{Br}
\end{align*}
\]

(65) \hspace{1cm} (64)

The mechanism by which 64 was converted to 104 probably involves proton abstraction by \text{-}butoxide from the hydroxyl group with subsequent loss of benzaldehyde and formation of the corresponding phenyl anion. This anion should in fact possess a fair amount of stability as it is not only ortho to a halogen, but is on a ring with three additional halogens to help stabilize the negative center by induction. The anion can then acquire a proton from the solvent to give 104, and the benzaldehyde can undergo a Cannizzaro reaction to give benzyl alcohol and \text{-}butyl benzoate which is then saponified to benzoic acid upon addition of water to the reaction mixture.

Because it appeared that the alcohol (64) did not react with thionyl chloride at the temperatures used in Van Meter's procedure, the alcohol was stirred with thionyl chloride either at room temper-
ature or at reflux. The product, m.p. 164-165.5°, isolated in both cases was assigned the structure of 9,10-dihydro-9-phenyl-1,2,3,4-tetrabromoanthracene (97). The structure assignment was based primarily on the elemental analysis, nuclear magnetic resonance spectrum, and the fact that its reaction with N-bromosuccinimide afforded 9-phenyl-1,2,3,4-tetrabromoanthracene (98).

The nuclear magnetic resonance spectrum was particularly interesting. It showed the expected multiplet integrating for nine protons centering at about 7.2 δ which was attributed to the aromatic hydrogens. A singlet integrating for one proton appeared at 5.87 δ and this was assigned to the highly deshielded methine hydrogen. Van Meter reported that the methine hydrogen in 5,12-dihydro-9-phenyl-naphthacene (105) is seen at 5.32 δ. Recently, the nuclear magnetic resonance spectrum of 9,10-dihydro-9,10-diphenylanthracene (106) has been reported, and the methine hydrogens are stated as appearing at 5.28 δ.\(^{53}\) The extra downfield shift observed in the spectrum of 97 is undoubtedly due to the deshielding effect of the electronegative bromine atoms. Centering at 4.10 δ and integrating for two protons was an AB-quartet. The center of gravity of the lower field

doublet was calculated to be 4.39 δ and that of the higher field doublet, 3.81 δ with $J_{AB}=19$ cps. This was assigned to the two methylene hydrogens. In 105 the methylene hydrogens appear as a singlet at 3.94 δ. The implications of this are that at room temperature there is a rapid equilibrium between the two possible conformational isomers of 105 in which the nonplanar middle six-membered ring flips back and forth so that the 9-phenyl substituent is axial in one conformer (105a) and equatorial in the other (105b). The two nonequivalent methylene protons appear as a time-averaged singlet in the nuclear magnetic resonance spectrum. However, in 97 there apparently exists sufficient steric interaction between the 1-bromine and 9-phenyl substituents to prevent the equatorial 9-phenyl isomer (97b) from existing, at least at room temperature. Thus, only the isomer (97a) with the 9-phenyl group in the axial position is present and the two nonequivalent methylene protons split one another to appear as an AB-quartet in the nuclear magnetic resonance spectrum. This hypothesis was confirmed when molecular models were built using Leybold atom models, the relative dimensions of which are in accord with those obtained experimentally. The model of 9,10-dihydro-9-phenylanthracene (31) showed that the molecule could readily flip back and forth from one conformer to the other, provided the plane of the 9-phenyl group was perpendicular to that of the anthracene system. The model of the tetrabromodihydroanthracene (97) showed, however, that the conformer in which the 9-phenyl group was axial could not be transformed into the equatorial conformer. Indeed, construction of the equatorial conformer was impossible even when the plane of the
9-phenyl group was perpendicular to that of the anthracene system. Further inspection of the model of 97 led to the assignment of the equatorial methylene hydrogen to the lower field doublet because of its close proximity to the 4-bromo substituent and its position within the plane of the two benzene rings of the anthracene system. Because the 9-phenyl group was found to be twisted in such a manner that the axial methylene hydrogen sits somewhat over the ring's π-cloud, it was expected that this hydrogen should be shielded to a certain extent, and it was therefore assigned to the higher field doublet.

(105)  

(106)  

(105a)  

(105b)  

(97a)  

(97b)
Thus, it appeared from the chemical evidence that the alcohol (64) was too hindered to allow conversion by thionyl chloride to the \( \alpha \)-chloro derivative (65) at lower temperatures. However, at higher temperatures, where the chloride (65) could be formed, the conditions were too severe to permit the chloride's long-term existence and it rearranged with loss of hydrogen chloride to give the dihydroanthracene (97).

The other approach involving oxidation of the methylene group in 77 to a second carbonyl group was tried. The procedure used by Van Meter,\(^{41}\) where 2-benzoyl-3-benzynaphthalene (107) was treated with bromine under the influence of light to give on work-up 2,3-dibenzynaphthalene (108), was used here on 1-benzoyl-2-benzyl-3,4,5,6-tetabromobenzene (77). The product, 1,2-dibenzoyl-3,4,5,6-tetabromobenzene (88), m.p. 210-212°, was obtained crude in 54% yield. Its nuclear magnetic resonance spectrum showed a broad multiplet centering at about 7.68 for the aromatic hydrogens, but
showed no aliphatic proton absorption, and the infrared spectrum contained a strong carbonyl absorption at 6.0 μ.

Reaction of the diketone (88) with lithium aluminum hydride and treatment of the resulting oily product with acetic acid gave a bright yellow compound, C<sub>20</sub>H<sub>16</sub>Br<sub>4</sub>O, m.p. 211-215°, in 60% yield. Its infrared spectrum displayed no hydroxyl or carbonyl absorption. The structure assigned to this compound was that of 1,3-diphenyl-4,5,6,7-tetrabromoiso benzofuran (109). Unlike 1,3-diphenylisobenzofuran (55), 109 did not fluoresce upon exposure to ultraviolet light. Reaction of 109 with maleic anhydride gave the expected Diels-Alder adduct (110).

It appears that only partial reduction of the diketone (88) occurred with lithium aluminum hydride and the intermediate lactol formed lost water on treatment with acid to give the isobenzofuran (109).
All melting points are uncorrected. Microanalyses were determined by Midwest Microlab, Inc., Indianapolis, Indiana, and Alfred Bernhardt, Max-Planck Institute, Mülheim (Ruhr), Germany. The bromine determinations of certain compounds described in this section fall well outside the desired 0.3 limit of deviation from the calculated values. The explanation offered by Midwest Microlab, Inc. on this matter is that the "determination of halogen at this level [meaning the high bromine content encountered in most of the compounds described here] is quite difficult, the precision being a good deal less than for the usual percentages encountered."

3-Hydroxy-3-phenyl-4,5,6,7-tetrabromophthalide (72). — This synthesis was carried out using a modified procedure of Hofmann. A mixture of tetrabromophthalic anhydride (69) (500 g., 1.08 moles) and benzene (2.5 l.) were heated to 45° in a 5 l. 4-necked round-bottomed flask equipped with a thermometer, mechanical stirrer, and condenser. The heat source was removed and through the fourth neck was added anhydrous aluminum chloride (350 g., 2.6 moles) at a rate such as to maintain a temperature of 45-50° (25 minutes). The neck was stoppered, the reaction mixture heated at 48-50° for 30 minutes until the hydrogen chloride evolution had subsided, and refluxed for 5 hours. The mixture was cooled to 25° in an ice bath, a water-ice slush (500 g.) was added at a rate which kept the temperature from exceeding 35°.
followed by addition of concentrated hydrochloric acid (100 ml.). The solvent (1850 ml.) was removed by distillation and the residue washed with four 2.5-l. portions of 5% hydrochloric acid and one 2.5-l. portion of water, filtering after each washing. The solid was dried in air, taken up in boiling tetrahydrofuran, the solution filtered, concentrated, and refrigerated for several days. Filtration gave crystals (539 g., 92%), m.p. 237-240°. Several recrystallizations from tetrahydrofuran-benzene of a small portion gave the analytic sample, m.p. 238-240° (lit., 250-252°).

Attempted Hydrogenation of 3-Hydroxy-3-phenyl-4,5,6,7-tetrabromo-phthalide (72). — A mixture of the 3-hydroxyphthalide (72) (5.0 g., 0.0092 mole), 5% palladium on carbon (1.5 g.), dioxane (30 ml.), and glacial acetic acid (30 ml.) were shaken under 46 psi of hydrogen for 22 hours. The filtered solution was poured into 6 N hydrochloric acid (200 ml.), allowed to stand for one hour, and the solid isolated on filtration was recrystallized from tetrahydrofuran-n-hexane to give starting hydroxyphthalide 72 (4.0 g., 80%), m.p. 133-137°, whose infrared spectrum was identical to that of the starting material (72).

Hydrogenation of Sodium 2-benzoyl-3,4,5,6-tetramobromobenzoate (78). — To a solution of 3-hydroxy-3-phenyl-4,5,6,7-tetramobromophthalide (72) (5.0 g., 0.0092 mole) in dioxane (60 ml.) was added 0.21 M aqueous sodium hydroxide (44 ml., 0.0093 mole) and the resulting solution boiled briefly to ensure complete salt formation. To the cooled solution was added 5% palladium on carbon (1.5 g.) and the mixture was shaken under an initial pressure of 46 psi of hydrogen. After 15 minutes, the pressure was increased back to 46 psi and shaken for
another 5 hours. The filtered solution was poured into 6 N hydro-
chloric acid (500 ml.) and after standing overnight, the solid ob-
tained on filtration was recrystallized from tetrahydrofuran-cyclo-
hexane to give white feathery needles (0.72 g., 37%), m.p. 113-115°
(lit., 54 114°, uncorr.), whose infrared spectrum was identical with
that of authentic o-benzylbenzoic acid (79). A second crop of crystals (0.55 g.) was obtained.

3-Phenyl-4,5,6,7-tetra bromophthalide (81). -- To a warm solution
of 3-hydroxy-3-phenyl-4,5,6,7-tetra bromophthalide (72) (300 g., 0.554
mole) in tetrahydrofuran (6 l.) contained in a 12 l. 3-necked round-
bottomed flask equipped with a condenser and mechanical stirrer was
added 2% aqueous sodium hydroxide (1.5 l.) and sodium borohydride
(8.5 g.). After stirring at room temperature for 20 hours, the reac-
tion mixture was brought almost to neutrality with 6 N hydrochloric
acid (47 ml.). Sodium borohydride (5.5 g.) was added, the mixture
stirred at room temperature for 9.5 hours, the temperature taken up to
50°, and sodium borohydride added in three 3-g. portions at 12-hour
intervals. To the still-warm reaction mixture was added 6 N hydro-
chloric acid and the tetrahydrofuran (5.8 l.) was distilled from the
mixture while water was added in 1000-ml. portions to keep the volume
of the mixture constant. The resulting mixture consisted of a light
brown solid mass covered with a layer of shiny white platelets which
were easily rinsed into a Büchner funnel leaving the brownish mass
undisturbed. The white solid (113 g.) was identical with sodium

54 F. Rotering and Th. Zincke, Ber., 2, 631 (1876).
2-benzy01-3,4,5,6-tetabromobenzoate (78) which was prepared from 3-
hydroxy-3-phenyl-4,5,6,7-tetabromophthalide (72) and sodium carbonate.
The brownish solid was dried and recrystallized from tetrahydrofuran
to give the crude phthalide (81) (95 g., 95%), m.p. 228-231°. Sev-
eral recrystallizations of a small portion from chloroform gave the
analytical sample as white short needles, m.p. 231-233°.
Anal. Calcd. for C_{14}H_{8}Br_{9}O_{2} (525.9): C, 31.98; H, 1.15; Br, 60.79.
Found: C, 32.01; H, 1.17; Br, 60.86.

Attempted Hydrogenation of 3-Phenyl-4,5,6,7-tetabromophthalide
(81). — A mixture of the phthalide (81) (5.00 g., 0.00956 mole), 5%
palladium on carbon (1.5 g.), dioxane (125 ml.), and absolute ethanol
(100 ml.) was shaken under 35 psi of hydrogen for 20 hours. The fil-
tered solution was concentrated to 100 ml., poured into 5% hydro-
chloric acid (400 ml.), and allowed to stand for a day. The solid
obtained on filtration was recrystallized from chloroform-cyclo-
hexane to afford crystals of starting phthalide (81) (2.1 g.), m.p.
212-224°, whose infrared spectrum was identical with that of the
starting material (81).

3-Chloro-3-phenyl-4,5,6,7-tetabromophthalide (83). — A mixture
of 3-hydroxy-3-phenyl-4,5,6,7-tetabromophthalide (72) (20.0 g.,
0.0369 mole), thionyl chloride (8.8 g., 0.074 mole), N,N-dimethyl-
formamide (3.0 g.), and chlorobenzene (200 ml.) was heated on a steam
bath for 45 minutes. The solvent was removed in vacuo with a rotary
evaporator and the solid residue recrystallized from tetrahydrofuran
to give crystals (14.8 g., 71%), m.p. 241-250°. Several recrystall-
zations of a small portion from chloroform gave the analytical sample,
Hydrogenation of 3-Chloro-3-phenyl-4,5,6,7-tetrabromophthalide (83). — A mixture of the 3-chlorophthalide (83) (5.0 g., 0.0089 mole), 5% palladium on carbon (1.5 g.), and dioxane (125 ml.) was shaken under an initial pressure of 40 psi of hydrogen for 10 hours, the pressure increased back to 40 psi, and shaken for 4 hours more. The filtered reaction mixture was stripped of solvent with a rotary evaporator, and the white solid residue recrystallized from chloroform to give short white needles of 3-phenyl-4,5,6,7-tetrabromophthalide (81) (1.8 g., 38%), m.p. 235-236°. A second crop of crude crystals (0.5 g.) was obtained.

Reaction of 3-Phenyl-4,5,6,7-tetrabromophthalide (81) with Zinc. — A mixture of the phthalide (81) (1.00 g., 0.00190 mole), zinc dust (4.4 g., 0.067 mole), glacial acetic acid (100 ml.), and concentrated hydrochloric acid (5 ml.) was stirred magnetically at room temperature for 30 minutes and then heated on a steam bath for 2.5 hours. The mixture was taken up in benzene and the benzene solution washed with water and dried over anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator under reduced pressure and the solid residue recrystallized from chloroform to give crystals (0.2 g., 29%), m.p. 184-185.5°.

Anal. Calcd. for C_{14}H_{8}Br_{4}O_{2} (368.0): C, 45.68; H, 2.19; Br, 43.42.
3,3-Diphenyl-4,5,6,7-tetrabromophthalide (89). — A mixture of 3-chloro-3-phenyl-4,5,6,7-tetrabromophthalide (83) (1.00 g., 0.00179 mole), anhydrous aluminum chloride (0.4 g., 0.003 mole), and benzene (50 ml.) were refluxed for 2.75 hours. To the cooled reaction mixture was added water (20 ml.) with vigorous stirring, the mixture transferred to a separatory funnel, and benzene (60 ml.) added. The mixture was washed with two 50-ml. portions of 6 N hydrochloric acid and five 100-ml. portions of water, filtered through anhydrous magnesium sulfate, and the solvent removed with a rotary evaporator under reduced pressure to give a yellowish solid residue (0.99 g., 92%), m.p. 250-272°. Several recrystallizations from chloroform gave the analytical sample as white crystals, m.p. 279-281°.

Anal. Calcd. for C26H16Br8O2 (602.0): C, 39.90; H, 1.68; Br, 55.11.

Found: C, 39.78; H, 1.70; Br, 55.38.

3,4,5,6-Tetrabromo-o-xylene (70). — This synthesis was carried out using a slightly modified procedure of Hennion and Anderson.51 To a mixture of bromine (500 ml., 9.8 moles), iron powder (42 g., 0.72 mole), and cyclohexane (1 l.) contained in a 3 l. 3-necked round-bottomed flask immersed in ice and equipped with a hydrogen bromide exit tube, mechanical stirrer, and an adding funnel charged with o-xylene (200 ml., 1.66 moles), was slowly added the o-xylene over a period of 6.5 hours. After stirring for an additional 2 hours, the excess bromine was removed under reduced pressure with a water aspirator. The crude solid was extracted with benzene in a Soxhlet apparatus and crystallized from the benzene to give white needles
(458 g., 65%), m.p. 260-262°. A second crop (179 g.) was obtained. A small portion of the first crop was recrystallized from chloroform to give the analytical sample, m.p. 261.5-263° (sealed capillary) (lit., 260-261°).

\[ \text{a, a', 3, 4, 5, 6-Hexabromo-o-xylene (93).} \]

A solution of 3, 4, 5, 6-tetrabromo-o-xylene (70) (100 g., 0.237 mole) in carbon tetrachloride (3 l.) contained in a 5 l. 3-necked round-bottomed flask equipped with a condenser, mechanical stirrer, and adding funnel charged with a solution of bromine (78.0 g., 0.487 mole) in carbon tetrachloride (200 ml.) was stirred, refluxed, and irradiated with a General Electric 275 W sunlamp while the bromine solution was added over 1.5 hours. Irradiation and reflux was continued for an additional 15 minutes, the solvent removed with a rotary evaporator under reduced pressure, and the solid residue crystallized from chloroform to give white crystals (120 g., 88%), m.p. 165-166°. A small portion was recrystallized from chloroform to give the analytical sample, m.p. 166-167.5°.

**Anal.** Calcd. for C$_9$H$_4$Br$_6$ (579.6): C, 16.58; H, 0.69; Br, 82.73.

*Found:* C, 16.73; H, 0.94; Br, 82.58.

\[ \text{1, 2-Dibenzyl-3, 4, 5, 6-tetrabromobenzene (60).} \]

A mixture of a, a', 3, 4, 5, 6-hexabromo-o-xylene (93) (55.0 g., 0.0948 mole), anhydrous ferric chloride (2.0 g., 0.012 mole), and benzene (1 l.) was refluxed for 7.3 hours. To the cooled reaction mixture was added water (250 ml.) with vigorous stirring followed by addition of benzene (500 ml.). The mixture was transferred to a 3 l. separatory funnel, the aqueous layer drawn off, the organic layer washed with five 500-ml. portions of water, and filtered through anhydrous magnesium sulfate. The benzene was removed with a rotary evaporator under reduced
pressure and the solid residue crystallized from chloroform to give crystals (41.9 g., 72%), m.p. 220-225°C. A small portion was recrystallized twice from chloroform to give the analytical sample as white short needles, m.p. 219-221°C; ultraviolet spectrum: \( \lambda_{\text{max}} \) dioxane 225 mp (log \( \epsilon \) = 4.89), 240 sh (4.38), 265 sh (3.68).

Anal. Caled. for C\(_{30}\)H\(_{14}\)Br\(_4\) (574.0): C, 41.85; H, 2.46; Br, 55.69.
Found: C, 41.59; H, 2.34; Br, 56.09.

**Attempted Conversion of 1,2-Dibenzyl-3,4,5,6-tetrabromobenzene (60) to 1,2-Diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59).** — A mixture of 1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60) (2.00 g., 0.00348 mole), \( \text{N-bromosuccinimide} \) (0.66 g., 0.0037 mole), and carbon tetrachloride (50 ml.) was refluxed and irradiated with a General Electric 300 W tungsten filament lamp for 30 minutes. The mixture was cooled, filtered, and the filtrate stripped of solvent with a rotary evaporator under reduced pressure. The yellow crystalline residue was taken up in benzene (25 ml.) and a solution of 14% potassium \( \text{t-butoxide} \) in \( \text{t-buty alcohol} \) (50 ml.) added. The mixture was refluxed for one hour. The brown mixture was diluted with benzene (100 ml.), washed with five 100-ml. portions of water, filtered through anhydrous magnesium sulfate and evaporated to a volume of 15 ml. with a rotary evaporator under reduced pressure. Filtration afforded tan crystals (0.501 g.) whose infrared spectrum was identical to that of the starting material (60). The mother liquor was chromatographed through grade N I alumina eluting with benzene. Evaporation of the eluate gave yellow crystals (0.753 g.) of starting dibenzylbenzene (60). Further elution of the column failed to produce any more
crystalline material.

Reaction of 1,2-Dibenzyl-3,4,5,6-tetrabromobenzene (60) with N-Bromosuccinimide. — A mixture of the dibenzylbenzene (60) (2.00 g., 0.00348 mole), N-bromosuccinimide (1.61 g., 0.00905 mole), and carbon tetrachloride (100 ml.) was refluxed and irradiated with a General Electric 275 W sunlamp for 30 minutes. The orange mixture was cooled and filtered. The filtrate was stripped of solvent with a rotary evaporator under reduced pressure and the residue chromatographed through grade N I alumina with 1:1 chloroform-cyclohexane. The yellow band was collected and the eluate evaporated to give 9-phenyl-1,2,3,4-tetrabromoanthracene (98) as yellow crystals (0.77 g., 59%), m.p. 222-223°; ultraviolet spectrum: \( \lambda_{\text{max}} \) dioxane 215 mp(\( \log e = 4.40 \)), 233(4.34), 268sh(4.76), 372(3.73), 392(3.90), 412(3.83).

Anal. Calcd. for C\(_{26}\)H\(_{16}\)Br\(_4\): C, 42.14; H, 1.76; Br, 56.09.

Found: C, 42.12; H, 1.87; Br, 56.34.

Reductive Debrumination of 9-Phenyl-1,2,3,4-tetrabromoanthracene (98). — A mixture of the anthracene (98) (0.200 g., 0.000361 mole), 10% palladium on carbon (0.10 g.), triethylamine (100 ml.), and benzene (200 ml.) was shaken under an initial pressure of 40 psi of hydrogen for 2 hours. The filtered reaction mixture was stripped of solvent with a rotary evaporator under reduced pressure to give a yellow oil which was chromatographed twice through grade N I alumina eluting with 1:1 benzene-cyclohexane, following the leading fluorescent band with an ultraviolet lamp. This fluorescent band was collected on the second chromatographing and the solvent removed with a rotary evaporator to give a pale yellow oil which solidified on
standing for several hours. Recrystallization from absolute ethanol gave pale yellow crystals (0.015 g., 16%), m.p. 146-151°. Another recrystallization from absolute ethanol gave almost-white shiny platelets of 9-phenylanthracene (47), m.p. 149-151° (lit., \(^{55}\) 152-153°), whose infrared spectrum was identical with that of an authentic sample.

1,2-Bis(p-benzenesulfonylbenzyl)-3,4,5,6-tetrabromo benzene (99).

A mixture of 1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60) (25.0 g., 0.0436 mole), benzenesulfonyl chloride (250 ml.), and anhydrous aluminum chloride (20.0 g., 0.150 mole) was stirred magnetically in a 500 ml. round-bottomed flask immersed in an oil bath at 80° for 3 hours. The flask was then immersed in an ice bath, water (100 ml.) slowly added, the mixture poured into a solution of 10% aqueous sodium hydroxide (500 ml.) and methanol (500 ml.), and heated on a steam bath for 1 hour. The pink solid was removed by filtration and washed with 3 N hydrochloric acid followed with water. The air-dried solid was taken up in hot chloroform (500 ml.), treated with activated charcoal (7 g.), filtered, and concentrated with gradual addition of methanol to give white short needles (29.9 g., 79%), m.p. 265-269° (became semiliquid at 140° and completely resolidified by 165°). The infrared spectra of the unmelted and recrystallized melted material were identical. Two more recrystallizations of a small portion from chloroform-methanol gave the analytical sample, m.p. 140-165° and 269-270°; ultraviolet spectrum: \(\lambda_{\text{max}}\) dioxane 219 mp.

\(^{55}\) A. Baeyer, Ann., \(202\), 36 (1880).
(log $\epsilon$=4.89), 242(4.86), 273sh(3.78).

**Anal. Calcd. for C$_{32}$H$_{28}$Br$_4$O$_4$S$_2$ (854.3):** C, 44.98; H, 2.60; Br, 37.42; S, 7.51.

**Found:** C, 44.93; H, 2.82; Br, 37.62; S, 7.41.

7-Benzensulfonyl-9-(p-benzenesulfonylphenyl)-1,2,5,4-tetrabromoanthracene (100). — A mixture of 1,2-bis(p-benzenesulfonylbenzyl)-1,2,5,4-tetrabromobenzene (99) (1.00 g., 0.00117 mole), bromine (0.55 g., 0.0028 mole), and carbon tetrachloride (200 ml.) was refluxed and irradiated with a General Electric 275 W sunlamp for 3 hours. The reaction mixture was cooled and filtered to give a yellow solid (0.59 g., 60%), m.p. 252-255°. The filtrate yielded additional material (0.20 g.). Recrystallization of the first crop from chloroform-methanol gave the analytical sample as greenish yellow needles, m.p. 252-253.5°; ultraviolet spectrum: $A_{\text{max}}$ 216 mp (log $\epsilon$=4.60), 245(4.56), 286(4.97), 360sh(4.54), 380sh(3.76), 400(3.88), 422(3.85).

**Anal. Calcd. for C$_{32}$H$_{18}$Br$_4$O$_4$S$_2$ (850.3):** C, 45.20; H, 2.13; Br, 37.60; S, 7.54.

**Found:** C, 44.98; H, 2.00; Br, 37.90; S, 7.34.

Attempted Oximation of 1,2-Bis(p-benzenesulfonylbenzyl)-3,4,5,6-tetrabromobenzene (99). — To a mixture of 99 (1.00 g., 0.00117 mole), 14% potassium t-butoxide in t-butyl alcohol (3.8 ml.), and N,N-dimethylformamide (25 ml.) was added n-butyl nitrite (0.27 g., 0.0026 mole), whereupon the deep purple solution turned brown, and was stirred for 12 hours. The mixture was poured into water (250 ml.),
concentrated hydrochloric acid (5 ml.) added, and the solid obtained on filtering was dried to give crude crystals (0.89 g.), whose infrared spectrum was identical with that of the starting material (99).

3,4,5,6-Tetramono-o-toluic Acid (73). — To a magnetically stirred mixture of bromine (1 l.) and anhydrous aluminum chloride (270 g., 2.00 moles) contained in a 2 l. round-bottomed flask immersed in an ice bath was gradually added o-toluic acid (100.0 g., 0.735 mole). The flask was fitted with two condensers connected in tandem and the ice bath removed. The mixture was stirred for 1 hour and then refluxed for 20 hours. The bromine was removed by distillation until the mixture became very viscous and the rest of the bromine removed under reduced pressure. To the hard cake remaining were added water (1 l.) and concentrated hydrochloric acid (200 ml.). The cake was broken up with a spatula, the mixture filtered, the solid collected washed with 7% aqueous sodium bisulfite solution (400 ml.) followed with water, and dried to give the product (328 g., 99%), m.p. 230-236°. Three recrystallizations of a small portion from chloroform gave colorless rhombs, m.p. 236-237°.

Anal. Calcd. for C₉H₄Br₄O₂ (451.8): C, 21.27; H, 0.89; Br, 70.76.

Found: C, 21.40; H, 0.97; Br, 71.52.

3,4,5,6-Tetramono-o-toluyl chloride (101). — A mixture of 3,4,5,6-tetramono-o-toluic acid (73) (300 g., 0.664 mole), thionyl chloride (119 g., 1.00 mole), N,N-dimethylformamide (5.0 g., 0.068 mole), and benzene (2.5 l.) was refluxed for 4 hours. The solvent was removed by distillation under reduced pressure, the solid residue taken up in chloroform (1.5 l.), the solution filtered, and the sol-
vent removed from the filtrate with a rotary evaporator under reduced pressure to give tan colored product (304 g., 97%), m.p. 126-129°. A small portion was recrystallized several times from cyclohexane to give the analytical sample as white crystals, m.p. 128.5-130.5°.

Anal. Calcd. for C_{6}H_{3}Br_{4}ClO (470.2): C, 20.43; H, 0.64; total halogen calculated as Br, 84.98.

Found: C, 20.71; H, 0.58; total halogen calculated as Br, 85.09.

2-Benzoyl-3,4,5,6-tetrabromotoluene (102). — A mixture of 3,4,5,6-tetrabromo-o-tolyl chloride (101) (500 g., 0.658 mole), anhydrous aluminum chloride (101 g., 0.757 mole), and benzene (2 l.) was first mechanically stirred at room temperature for 15 minutes, then refluxed for 2 hours. The flask was immersed in an ice bath, and water (500 ml.) added with vigorous stirring. The mixture was transferred to a 4 l. separatory funnel, the aqueous layer drawn off, the organic layer washed with one 1-l. portion of 6 N hydrochloric acid followed with seven 1-l. portions of water, dried over anhydrous magnesium sulfate, and the solvent removed with a rotary evaporator under reduced pressure to give tan solid product (320 g., 96%), m.p. 158-161°. A small portion was recrystallized twice from chloroform-methanol to give the analytical sample as glistening white prisms, m.p. 162-163.5°.

Anal. Calcd. for C_{14}H_{8}Br_{4}O (511.9): C, 32.84; H, 1.57; Br, 62.45.

Found: C, 32.77; H, 1.64; Br, 62.48.

2-Benzoyl-a,3,4,5,6-pentabromotoluene (103). — A mixture of 2-benzoyl-3,4,5,6-tetrabromotoluene (102) (300 g., 0.586 mole), bromine
(96.0 g., 0.600 mole), and carbon tetrachloride (8 l.) was refluxed and irradiated with three General Electric 275 W sunlamps for 70 hours. The solvent was removed by distillation under reduced pressure until a volume of about 400 ml. was reached and the remaining solvent was removed with a rotary evaporator. The brown-black liquid residue was taken up in cyclohexane (750 ml.) and crystallization induced by scratching. After standing for one day, the mother liquor was removed by decantation, the remaining crust was broken up and washed with n-pentane to give tan crystals (244 g., 71%), m.p. 132-140°. Several recrystallizations of a small portion from cyclohexane gave the analytical sample as nearly white crystals, m.p. 143.5-145°.

Anal. Calcd. for C_{14}H_{9}Br_{8}O (590.8): C, 28.45; H, 1.19; Br, 67.64.

Found: C, 28.55; H, 1.28; Br, 66.35.

1-Benzoyl-2-benzyl-3,4,5,6-tetrabromobenzene (77). — A mixture of 2-benzoyl-a,3,4,5,6-pentabromotoluene (103) (244 g., 0.413 mole), anhydrous aluminum chloride (67 g., 0.50 mole), and benzene (3 l.) was refluxed for 3 hours. The flask was immersed in an ice bath and 3 N hydrochloric acid (1 l.) was added with vigorous stirring. The mixture was transferred to a 6 l. separatory funnel, the aqueous layer drawn off, the organic layer washed with four 1-l. portions of water, and dried over anhydrous magnesium sulfate. The solvent was removed with a rotary evaporator under reduced pressure, and the brown liquid residue was taken up in cyclohexane (500 ml.). Crystallization was initiated by scratching, the solution refrigerated for 4 hours, the mother liquor removed by decantation, and the remaining crystals washed with n-pentane to give, after drying, tan
crystals (142 g.). A second crop (36.1 g.) was obtained from a combined mixture of mother liquor and washings. The two crops were combined and recrystallized from chloroform-cyclohexane to give light tan crystals (161 g., 66%), m.p. 135-150°. Several recrystallizations of a small portion from chloroform-ethanol gave the analytical sample as white crystals, m.p. 155-156°.

Anal. Calcd. for C_{26}H_{18}Br_{6}O (588.0): C, 40.85; H, 2.06; Br, 54.37.

Found: C, 40.72; H, 2.08; Br, 54.31.

1-Benzyl-2-(a-hydroxybenzyl)-3,4,5,6-tetraphenylbenzene (64). — A solution of 1-benzoyl-2-benzyl-3,4,5,6-tetraphenylbenzene (77) (25.0 g., 0.0426 mole) in benzene (125 ml.) and ether (100 ml.) was cooled to 0° and lithium aluminum hydride (1.6 g., 0.042 mole) was added while stirring magnetically. The reaction flask was capped with a calcium chloride drying tube, the mixture stirred at 0° for 15 minutes, the ice bath removed, and stirred for an additional 30 minutes. A 10% aqueous sodium hydroxide solution (10 ml.) was added dropwise, the mixture stirred for 30 minutes, filtered through anhydrous magnesium sulfate, and the solvent removed with a rotary evaporator under reduced pressure to give a crude white solid residue (23.6 g.). Recrystallization from benzene gave white crystals (12.7 g., 56%), m.p. 189-200°. A second crop (1.3 g.), m.p. 180-186°, was obtained from the mother liquor. Several recrystallizations of a small portion of the first crop from chloroform gave the analytical sample, m.p. 207-208.5°.

Anal. Calcd. for C_{26}H_{14}Br_{4}O (590.0): C, 40.71; H, 2.39; Br, 54.19.

Found: C, 40.48; H, 2.35; Br, 53.91.
Attempted Conversion of 1-Benzyl-2-(a-hydroxybenzyl)-3,4,5,6-tetrabromobenzene (64) to 1,2-Diphenyl-3,4,5,6-tetrabromobenzocyclobutene (59). — A 100 ml. round-bottomed flask containing the alcohol (64) (1.00 g., 0.00170 mole) was immersed in an ice-acetone bath. After a few minutes, thionyl chloride (40 ml.) precooled to 0° was added, the mixture was swirled in the ice-acetone bath for 5 minutes, the bath removed, and the mixture allowed to warm to room temperature with intermittent swirling. From the resulting clear solution was removed the thionyl chloride under reduced pressure with a rotary evaporator, the temperature not being permitted to exceed room temperature. The residual white crust coating the inner walls of the flask was rinsed with four 15-ml. portions of n-pentane followed by a final drying with a rotary evaporator. Into the flask containing the dried white solid was added a 14% solution of potassium t-butoxide in t-butyl alcohol (15 ml.) and benzene (40 ml.). The mixture was refluxed for 2.5 hours. The orange turbid mixture was washed with four 50-ml. portions of water, dried over anhydrous magnesium sulfate, filtered, and stripped of solvent with a rotary evaporator to give a pale yellow oily residue (0.428 g.). Addition of a few mls. of cyclohexane and scratching afforded crude crystals which were recrystallized from cyclohexane to give stubby needles of 2,3,4,5-tetrabromodiphenylmethane (104) (0.128 g., 16%), m.p. 75.5-77°.

Anal. Calcd. for C_{18}H_{14}Br_{5} (483.9): C, 32.26; H, 1.67; Br, 66.03.

Found: C, 32.50; H, 1.69; Br, 66.03.

Reaction of 1-Benzyl-2-(a-hydroxybenzyl)-3,4,5,6-tetrabromobenzene (64) with Potassium t-butoxide. — A mixture of the alcohol
(64) (0.375 g., 0.000636 mole), a 14% solution of potassium t-butoxide in t-butyl alcohol (15 ml.), and benzene (15 ml.) was refluxed for 6 hours. The brown turbid mixture was diluted with benzene (25 ml.), washed with five 50-ml. portions of water (the first three washings were combined and saved), dried over anhydrous magnesium sulfate, and stripped of solvent under reduced pressure with a rotary evaporator to give a yellow oil. The odor of benzaldehyde was prevalent. The material was chromatographed through grade N I alumina with benzene-cyclohexane (1:1). The eluate was stripped of solvent, the oily residue taken up in cyclohexane (2 ml.), n-pentane (4 ml.) added, and the solution refrigerated for 3 days. The mother liquor was removed from the crystals formed by decantation, the crystals washed with n-pentane, and dried to give white stubby needles (0.059 g., 19%), m.p. 75.5-77°, whose infrared spectrum was identical with that of 2,3,4,5-tetrabromodiphenylmethane (104). The retained aqueous washings mixture was treated with 6 N hydrochloric acid (10 ml.). The precipitate formed was extracted with chloroform (50 ml.), the extract dried by simply filtering it, the solvent removed under reduced pressure with a rotary evaporator, and the semisolid residue extracted with hot water. The water extract was concentrated by boiling to give on cooling crystals of benzoic acid (0.009 g., 23%), m.p. 118-120° (lit.,56 121.4°), whose infrared spectrum was identical with that of an authentic sample.

9,10-Dihydro-9-phenyl-1,2,3,4-tetrabromoanthracene (97). -- The

56 H. Kopp, Ann., 24, 257 (1855).
dihydroanthracene derivative (97) was prepared from 1-benzyl-2-(α-hydroxybenzyl)-3,4,5,6-tetrabromobenzene (64) and thionyl chloride under two different sets of reaction conditions which are described here.

1) A mixture of the alcohol (64) (0.500 g., 0.000847 mole) and thionyl chloride (15 ml.) was stirred at room temperature for 4.5 hours. Thin layer chromatography indicated only one compound present which was not the starting alcohol. The excess thionyl chloride was removed under reduced pressure with a rotary evaporator, not allowing the temperature to rise above 35°. The residue was treated three times with a 10-ml. portion of chloroform, which was removed with a rotary evaporator after each time. The resulting oil was chromatographed through grade N I alumina eluting with chloroform-cyclohexane (1:1). The eluate was evaporated on a rotary evaporator and the light yellow oil remaining crystallized from cyclohexane to give colorless short needles (0.264 g., 55%), m.p. 163-165.5°. Thin layer chromatography indicated it to be the same material present in the reaction mixture prior to work-up. Recrystallization from cyclohexane gave the analytical sample, m.p. 164-165.5°.

2) A mixture of the alcohol (64) (5.00 g., 0.00847 mole) and thionyl chloride (40 ml.) was refluxed for 1 hour. The excess thionyl chloride was removed under reduced pressure with a rotary evaporator, the residue treated two times with cyclohexane which was removed with a rotary evaporator, after each time. The residue was taken up in 15 ml. of cyclohexane whereupon crystallization occurred to give white crystals (3.88 g., 80%), m.p. 152-157°. A second crop was also
obtained (0.40 g.).

Anal. Calcd. for C_{28}H_{18}Br_{4} (572.0): C, 41.99; H, 2.12; Br, 55.89.

Found: C, 42.19; H, 2.31; Br, 55.81.

9-Phenyl-1,2,3,4-tetrabromoanthracene (98) from 9,10-Dihydro-9-phenyl-1,2,3,4-tetrabromoanthracene (97). — A mixture of the dihydroanthracene (97) (1.00 g., 0.00175 mole), N-bromosuccinimide (0.41 g., 0.0023 mole), and carbon tetrachloride (20 ml.) was refluxed and irradiated with a Sylvania 200 W tungsten filament lamp for 1.5 hours. The cooled mixture was filtered and the filtrate stripped of solvent with a rotary evaporator to give an orange solid residue (1.04 g.). The solid was chromatographed through grade N I alumina eluting with benzene and the eluate was evaporated with a rotary evaporator to give a yellow solid residue (0.80 g., 80%), m.p. 114-117°. Several recrystallizations from chloroform-methanol gave yellow crystals, m.p. 222-225°, whose infrared spectrum was identical with that of 9-phenyl-1,2,3,4-tetrabromoanthracene (98) prepared earlier from 1,2-dibenzyl-3,4,5,6-tetrabromobenzene (60).

1,2-Dibenzoyl-3,4,5,6-tetrabromobenzene (88). — A mixture of 1-benzoyl-2-benzyl-3,4,5,6-tetrabromobenzene (77) (25.0 g., 0.0426 mole), bromine (5.1 ml., 0.10 mole), carbon tetrachloride (300 ml.), and water (1 ml.) was refluxed and irradiated with General Electric 275 W sunlamp for 70 hours. The mixture was washed with two 200-ml. portions of 2% aqueous sodium thiosulfate solution followed by five 200-ml. portions of water. The washed organic solution was dried over anhydrous magnesium sulfate, the solvent removed under reduced pressure with a rotary evaporator, and the brown viscous oil remaining crys-
tallized from benzene-ethanol to give yellow crystals (13.7 g., 54%), m.p. 194-205°. The material was chromatographed through grade N I alumina eluting with benzene. The solvent was removed from the eluate with a rotary evaporator and a small portion of the residue recrystallized from chloroform-methanol to give the analytical sample as white needles, m.p. 210-212°.

**Anal. Calcd. for C_{28}H_{16}Br_{4}O_{2} (602.0):**

- C, 39.90; H, 1.67; Br, 53.11.
- Found: C, 39.87; H, 1.66; Br, 52.90.

**1,3-Diphenyl-4,5,6,7-tetrabromoiso benzofuran (109).** — A mixture of 1,2-dibenzoyl-3,4,5,6-tetrabromobenzene (88) (1.00 g., 0.00166 mole), lithium aluminum hydride (0.038 g., 0.0010 mole), benzene (15 ml.), and ether (15 ml.) was stirred magnetically at room temperature for 3 hours. The reaction was quenched with 10% aqueous sodium hydroxide solution (1 ml.), the mixture filtered through anhydrous magnesium sulfate, and the solvent removed under reduced pressure with a rotary evaporator to give a light yellow oily residue. To the oil was added glacial acetic acid (15 ml.), the mixture heated on a steam bath for 15 minutes, and the yellow crystals which separated removed by filtration and washed with methanol to give yellow feathery needles (0.580 g., 60%), m.p. 209-211.5°. A small portion was recrystallized from benzene-ethanol to give the analytical sample, m.p. 211-213°; ultraviolet spectrum: λ_{max} (dioxane 215 μμ(λ max = 4.43), 232(4.42), 273(4.46), 395(4.00).

**Anal. Calcd. for C_{28}H_{16}Br_{4}O (586.0):**

- C, 40.99; H, 1.72; Br, 54.56.
- Found: C, 41.06; H, 1.79; Br, 54.57.

**Adduct (110) from 1,3-Diphenyl-4,5,6,7-tetrabromoisobenzofuran**
(109) and Maleic anhydride. — A mixture of the isobenzofuran (109) (0.300 g., 0.000512 mole), maleic anhydride (0.11 g., 0.0011 mole), and toluene (15 ml.) was refluxed for 10 minutes. The white precipitate which had formed was collected upon filtration, washed with benzene and dried to give the Diels-Alder adduct (110) as white microcrystals (0.310 g., 89%), m.p. 290-302° (dec., began yellowing at 265°). A second crop (0.011 g.) was collected. Because of the extremely low solubility of the adduct in common organic solvents, recrystallization was not attempted.

Anal. Calcd. for C_{34}H_{28}Br_{4}O_{6} (684.0): C, 42.13; H, 1.77.

Found: C, 42.38; H, 1.77.
APPENDIX I: SOME NEW TETRABROMOBENZENE DERIVATIVES

During the course of this work a few new compounds were prepared which in themselves had no direct relevance to the problem at hand. They are reported here, however, to provide those who might be interested in them with the experimental details as to their preparations.

It was found that in the preparation of \(a,a',3,4,5,6\)-hexabromo-o-xylene (95) even when an excess of bromine was used, the reaction appeared to go cleanly to give the hexabromide (95) only. Indeed, when 95 was refluxed with bromine in carbon tetrachloride and irradiated with a sunlamp, no reaction took place. When refluxing carbon tetrachloride was replaced by refluxing o-dichlorobenzene as solvent, still no reaction occurred. Finally, reaction was induced when a melt of the hexabromide (95) at 260-265° was treated directly with bromine while irradiating the mixture with a sunlamp. The product, as determined by elemental analysis, isolated in 70% yield was \(a,a,a',a'-octabromo-o-xylene\) (111).

When the hexabromide (95) reacted with sodium sulfide in ethanol, the expected 1,3-dihydro-4,5,6,7-tetrabromoisothianaphthene (112) was isolated in 58% yield. Treatment of 112 with peracetic acid at room temperature gave 1,3-dihydro-4,5,6,7-tetrabromoisothianaphthene-2,2-dioxide (113) in 61% yield. 57

57 Preparation of the sulfone (113) was performed by Dr. M. J. Mitchell.
Cava and Deana have reported that when 1,3-dihydroisothianapthene-2,2-dioxide (114) was heated in refluxing diethyl phthalate, loss of sulfur dioxide took place and the only hydrocarbon isolated was 1,2,5,6-dibenzocyclooctadiene (115). However, when thermolysis of 114 was conducted over a hot wire in the gas phase, benzocyclobutene (54a) was obtained in good yield.

The explanation given for these results was that in solution the molecules of the intermediate α-xylylene (54b) formed upon loss of sulfur dioxide were in close enough proximity to one another and possessed sufficiently long lifetimes that they preferred to dimerize to give 115 rather than snap shut to give the four-membered ring in 54a. In the gas phase, however, the α-xylylene (54b) molecules were far enough apart that they were given enough time to close and give

When the sulfone (113) was heated in refluxing diethyl phthalate, loss of sulfur dioxide occurred and a compound, m.p. 220–221.5°, was obtained in 42% yield. The analysis and mass spectrum of the compound were consistent with the assigned structure of 3,4,5,6-tetra-bromobenzocyclobutene (116a).

These results as compared with those obtained by Cava and Deana indicate that the intermediate tetrabromo-ο-xylene (116b) has a shorter lifetime than does ο-xylene (54b) itself and cyclizes to give 116a rather than dimerizes. The reason for this may be attributed to the buttressing effect of the bromine atoms.
The experimental details for the new compounds described in this section are now given.

\(a, a', a', a', 3,4,5,6\text{-Octabromo-}o\text{-xylene (111)\text{.}}\) \(\rightarrow a, a', 3,4,5,6\text{-Hexabromo-}o\text{-xylene (95)}(50.0 \text{ g., 0.0865 mole})\) was placed in a 250 ml. 3-necked round-bottomed flask which was equipped with a condenser, mechanical stirrer, and an adding funnel with a pressure equalizing side-arm which was charged with bromine (50.0 g., 0.512 mole). The flask was immersed in a heat-treating salt bath preheated to 180°. The melted hexabromide was stirred and irradiated with a General Electric 275 W sunlamp while the temperature was gradually increased and bromine was added dropwise periodically. Hydrogen bromide began to evolve when the temperature reached about 250°. The temperature was raised to 260-265° and maintained there while the bromine was added in portions at such a rate (3.5 hours) as to prevent enough of it from building up in the system that bromine reflux took place (during addition of the last 10 g. of bromine, however, reflux did occur). After addition was complete, the reaction mixture was heated and irradiated for an additional five minutes, then cooled, and the excess bromine removed under reduced pressure. The dark solid residue was taken up in hot chloroform (2100 ml.), the solution treated with activated charcoal (50 g.), filtered, and boiled down to a volume of about 750 ml. After standing overnight, the crystals which formed were removed by filtration, washed with Skellysolve F and dried to give white prisms (44.7 g., 70%), m.p. 239-240.5°. A second crop of crystals (12.0 g.), m.p. 231-237°, was obtained.

Anal. Calcd. for C₉H₆Br₆ (737.5): C, 13.03; H, 0.27; Br, 86.69.
Found: C, 13.22; H, 0.30; Br, 86.66.

1,3-Dihydro-4,5,6,7-tetrabromoisothianaphthene (112). — A mixture of \(a, a', 3,4,5,6\)-hexabromo-\(p\)-xylene (93) (3.00 g., 0.00518 mole), well-ground sodium sulfide nonahydrate (1.25 g., 0.00521 mole), and absolute ethanol (150 ml.) was refluxed for 22 hours. The ethanol was removed under reduced pressure with a rotary evaporator and the solid residue taken up in benzene (125 ml.). The benzene solution was washed with four 100-ml. portions of water, dried over anhydrous magnesium sulfate and the solvent removed to give a solid residue (1.35 g., 58%), m.p. 209-215°. Several recrystallizations from benzene gave the analytical sample as pale yellow crystals, m.p. 214-216°.

Anal. Calcd. for \(C_8H_4Br_4S\) (451.9): C, 21.26; H, 0.89; Br, 70.75; S, 7.09.

Found: C, 21.57; H, 1.10; Br, 70.55; S, 7.25.

1,3-Dihydro-4,5,6,7-tetrabromoisothianaphthene-2,2-dioixide (113). 57 — A mixture of 1,3-dihydro-4,5,6,7-tetrabromoisothianaphthene (112) (1.82 g., 0.00403 mole), benzene (50 ml.), and 40% per-acetic acid (5 ml.) was stirred magnetically at room temperature for 4 days. The white precipitate was removed by filtration to give white solid (1.18 g., 61%), m.p. 250-255°. Two recrystallizations from \(N, N\)-dimethylformamide gave the analytical sample, m.p. 260-261°.

Anal. Calcd. for \(C_6H_4Br_4O_2S\) (483.9): C, 19.86; H, 0.83; Br, 66.07.

Found: C, 20.08; H, 0.94; Br, 66.25.

3,4,5,6-Tetrabromobenzo[cyclobutene (116a). — A mixture of 1,3-dihydro-4,5,6,7-tetrabromoisothianaphthene-2,2-dioixide (113) (1.00 g., 0.00207 mole) and diethyl phthalate (50 ml.) was refluxed for 7 hours.
The cooled mixture was poured into a solution of sodium hydroxide (24 g.) in water (200 ml.) and 95% ethanol (100 ml.). The mixture was heated on a steam bath with occasional stirring until it had evaporated to a volume of 200 ml. The precipitate was collected on filtration, washed with water, and sucked dry to give a tan solid (0.790 g.). The solid was chromatographed through grade N I alumina eluting with 5% chloroform in cyclohexane. The solvent was removed from the eluate under reduced pressure with a rotary evaporator to give white needles (0.362 g., 42%), m.p. 202-215°. Recrystallization from cyclohexane gave the analytical sample as colorless needles, m.p. 220-221.5° (sealed capillary). The mass spectrum showed the parent peak at m/e 420.

Anal. Calcd. for C₆H₄Br₄ (419.8): C, 22.89; H, 0.96; Br, 76.16.

Found: C, 23.25; H, 1.15; Br, 75.68.
APPENDIX II: INFRARED ABSORPTION SPECTRA

All infrared spectra were determined in pressed potassium bromide pellets with a Perkin-Elmer, Model 137, Sodium Chloride Spectrophotometer.
APPENDIX III: ULTRAVIOLET ABSORPTION SPECTRA

All ultraviolet spectra were determined in dioxane solution with a Perkin-Elmer, Model 202, Ultraviolet-Visible Spectrophotometer.
Wavelength, μm
APPENDIX IV: NUCLEAR MAGNETIC RESONANCE SPECTRA

All nuclear magnetic spectra were determined in deuteriochloroform solution with a Varian A-60 or A-60A NMR spectrometer using tetramethylsilane as an internal standard.