Studies in the Diphenylbutadiene series the Bromination and attempted reduction of 1-PARA-Carboxyphenyl--4-Phenylbutadiene 1,3

Daniel Wearring
Atlanta University

Follow this and additional works at: http://digitalcommons.auctr.edu/dissertations

Part of the Chemistry Commons

Recommended Citation
STUDIES IN THE DIPHENYLHUTADIENE SERIES
THE BROMINATION AND ATTEMPTED REDUCTION
OF 1-PARA-CARBOXYPHENYL-4-PHENYLHUTADIENE 1,3

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

BY
DANIEL WEARRING

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
JUNE, 1950
ACKNOWLEDGEMENT

The writer is sincerely grateful to Dr. K. A. Huggins, Chairman of the Department of Chemistry, Atlanta University, whose sincere interest, as exemplified by his kindly assistance and many valuable suggestions, was equally inspiring and helpful. Acknowledgements are also made to Dr. H. C. McBay, Department of Chemistry, Morehouse College for his suggestions.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Part</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. THEORETICAL</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>11</td>
</tr>
<tr>
<td>Preparation of Cinnamylidene Acrylic Acid</td>
<td>11</td>
</tr>
<tr>
<td>Preparation of l-p-Carboxyphenyl-4-Phenylbutadiene 1,3</td>
<td>11</td>
</tr>
<tr>
<td>Preparation of l-p-Carboxethoxyphenyl-4-Phenylbutadiene 1,3</td>
<td>11</td>
</tr>
<tr>
<td>Preparation of l-p-Carboxethoxyphenyl-4-Phenylbutadiene 1,3</td>
<td>11</td>
</tr>
<tr>
<td>Hydrolysis of l-p-Carboxethoxyphenyl-4-Phenylbutadiene</td>
<td>13</td>
</tr>
<tr>
<td>Bromination of l-p-Carboxyphenyl-4-Phenylbutadiene-1,3</td>
<td>15</td>
</tr>
<tr>
<td>Attempted Reduction of l-p-Carboxyphenyl-4-Phenylbutadiene 1,3</td>
<td>15</td>
</tr>
<tr>
<td>Ozonization of l-p-Carboxyphenyl-3,4-Dibromo-Phenyldiene</td>
<td>16</td>
</tr>
<tr>
<td>The Preparation of 1,2-Dihydroxy-3,4-Dibromo-1, p-Carboxyphenyl-4-Phenylbutane</td>
<td>17</td>
</tr>
<tr>
<td>The Cleavage of 1,2-Dihydroxy-3,4-Dibromo-1-p-Carboxyphenyl-4-Phenylbutane</td>
<td>18</td>
</tr>
<tr>
<td>Preparation of 1,2,3,4-Tetrabromo-1-p-Carboxyphenyl-4-Phenylbutane</td>
<td>19</td>
</tr>
<tr>
<td>III. SUMMARY</td>
<td>20</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>21</td>
</tr>
</tbody>
</table>
PART I

THEORETICAL

The object of this investigation was to determine the mode of addition of bromine to 1-p-carboxyphenyl-4-phenylbutadiene 1,3 in ethyl acetate as the solvent. It has been shown that substituted butadiene may add in the 1,2-, 1,4- or 3,4-positions. These findings may well be explained on the basis of "step-wise addition" as suggested by Lapworth. The positions of addition may be predicted with a knowledge of the behavior of the butadienoid compound and the addenda, but there are known cases where the predicted compound was not formed or was formed in small amounts with one of the isomeric forms being formed in greater yields, hence attempts to interpret the expected and observed behavior of the diene under study are included in this report.

There are three possible modes of addition of two bromine atoms to 1-p-carboxyphenyl-4-phenylbutadiene-1,3.

\[ \text{1,4 addition} \]

\[ \text{1,2 addition} \]

\[ \text{3,4 addition} \]

\[ \text{1Lapworth, J. Chem. Soc., 79, 1267 (1901).} \]
It was proposed to add a mole of bromine to the 1-p-carboxyphenyl-4-phenylbutadiene and to determine the positions of the addenda through ozonization of the product and the identification of the fragments.

1,4 addition

\[
\begin{align*}
&\text{Ozotization of a compound represented by Structure (I)} \\
&\text{followed by hydrolysis would yield } \alpha\text{-bromohomoterephthalic}
\end{align*}
\]
acid (m.p. unknown), and α-bromophenylacetic acid (m.p. 85°). Ozonization of a compound represented by structure (II) followed by hydrolysis would yield α-b-dibromo-b-phenylcarboxyl propionic acid (does not melt), and benzoic acid (m.p. 122°). Ozonization of a compound represented by structure (III) would give terephthalic acid, (sublimes c.a. 300°), and α-b-dibromo b-phenyl propionic acid (m.p. 195°).

No products that would have been derived from structures (I) or (II) were isolated. Terephthallic acid and α-b-dibromo b-phenyl propionic acid were isolated in experiments carried out by the process outlined above.

It is possible that the product isolated and identified might be the product of rearrangement or of isomerization of a 1,2- or 1,4- addition product. Ingold\(^2\) points out that unless special experimental precautions are taken the most stable products will be the one isolated, hence in the addition of bromine to a butadienoid system it is possible to have addition taking place in the 1,2-; 1,4- and 3,4- positions even though analysis of the final product gives evidence of only one mode of addition. The isolation of 1,2- addition product with only traces of (I) and (III) would however indicate that the 1,2- addition product is the most stable of the three possible products and that no rearrangement into a more stable form took place.

Wheland\textsuperscript{3} has pointed out that in the addition of bromine to a conjugated system the active reagent is probably a positive bromine ion, which is electrophilic. The point of the molecule at which an unshared pair of electrons can be provided most easily therefore becomes the point of attack for the active reagent.

\[(X)\quad (XI)\]

The structures (X) and (XI) indicate the manner in which the terminal carbon atoms may be brought to have an unshared pair of electrons. Addition of a reactive bromine ion to the systems (X) and (XI) give the initial products (XII) or (XIII) respectively.

\[(XII)\quad (XIII)\]

The activated complex (XII) can resonate among the structures (XII), (XIV), (XV); and the activated complex (XIII), can resonate\textsuperscript{3} among the structures (XIII), (XVI), and (XVII).

\[(XIV)\quad \text{Br}^+ \quad (XV)\]

\[(XVI)\quad \text{Br}^+ \quad (XVII)\]


\textsuperscript{3}Ibid., pp. 6-16.
The subsequent addition of the negative bromine ion to the initial product from (X) would produce 1,2- and 1,4- addition products while the addition of the negative bromine ion to the initial product from (XI) would produce 1,4- and 3,4- addition products.

Kharasch states that in unsymmetrical derivatives there is a definite "polarity" at the double bond of an ethylenic linkage. He formulated a mechanism in which the double bond is considered as consisting of an electron pair essentially normally situated and a second electron pair which is displaced away from the carbon atom bearing the most electronegative substituents. In systems represented as:

\[ R: \overset{\varepsilon}{C} : \overset{\varepsilon}{C} : R' \]  
\[ (XIX) \]

\[ R: \overset{\varepsilon}{C} : \overset{\varepsilon}{C} : R' \]  
\[ (XX) \]

group R is considered the more electronegative in a structure represented by (XIX) while in a structure represented by (XX), group R' is visualized as being the more electronegative of the two groups.

The relative "positions" of the second pair of electrons is determined by the relative electronegativities of the radicals attached to the double bond. The electron pair is displaced away from the carbon atom bearing the most

electronegative substituents and towards the opposite carbon atom. In a molecule of this nature the addition of HBr gives only one addition product; the acid halogen adds to the carbon atom from which the second electron pair is farthest displaced; the hydrogen ion attaches to the carbon atom to which the second electron pair is displaced.

\[
\begin{align*}
\text{H}_2\text{C} & - \text{H}_2\text{C}^- + \text{HBr} \rightarrow \text{H}_2\text{C} & - \text{H}_2\text{C}^-\text{OH} \\
\end{align*}
\]

The halogens and hypohalous acids are thought to be uniformly electrophillic when they behave as additive or substituting agents. Ingold postulated that when the halogen molecule is polarised by the local field of a solvent molecule, or of a surface on which adsorption has occurred, it is the electron depleted halogen atom which may be expected to be the more reactive. In an addition reaction under such conditions it may be supposed that \(\text{Br}^+\) is first bound with the rejection of \(\text{Br}^-\), which becomes accepted by the organic residue only as a consequence of the initial reaction. Ingold also concluded that the substituents or groups which activate anionotropic systems and promote aromatic hydrogen replacement by the ordinary substituting agents will increase the additivity of an ethylene towards reagents such as halogens the more active ions of which are positive.

\[5\text{Ingold, Chem. Rev., 15, 270 (1934).}\]
Ingold assumes that in halogen addition reactions under ordinary circumstances (non-ionising medium) the molecule, and not either of its ions, is the actual addition reagent. Under such conditions any 1,4- addition product would result from the rearrangement of the 1,2- isomer. He also assumes that in an ionising medium a distribution of the charge takes place after the initial addition of the positive bromide ion and "in a general case a mixture of bromides results, the composition of which will depend on the attached groups." He assumes that during the initial addition process, in an ionising medium, ions are formed and that "since the second bromine atom is liberated (as anion) only during the addition of the first, the initial product of addition...consists of the ions of the 1,2 dibromide." Experimental conditions determine the subsequent changes in the reaction process. In an ionising medium the initial product would more correctly be described as consisting of the ions of the 1,2- dibromide which may proceed by the simplified hypothetical mechanism:

\[
\text{Ions of } 1:2\text{-Bromide} \rightarrow \text{Ions of } 1:4\text{ Bromide} \rightarrow 1:4\text{ Bromide}
\]

The addition of various reagents; such as chlorine, bromine, hydrogen, etc., is further complicated by the possibility of cis-trans isomerism. Theoretically it is possible for 1-p-carboxyphenyl-4-phenylbutadiene-1,3 to exist in the following isomeric forms:
With the possibility of bromine adding cis or trans to each of the products one can see that a large number of products might easily be formed. Add to this the fact that the butenes formed may also exhibit geometrical isomerism one could predict that a large number of isomers would be formed under ordinary experimental conditions. Considering all of this the investigator was fortunate in isolating a single crystalline form which in all probability represented the most stable isomer. Our experimental work could give us very little information concerning the initial product or products of the reaction. In carrying out the ozonization experiments at the temperature of the salt-ice bath in the solvent in which it was formed we believe we were able to secure information as to which position isomers were formed. The 1,2-, 1,4- and 3,4- addition products would yield different fragments on ozonization and subsequent hydrolysis. However, it must be emphasized that our experiments were not
designed to lead to any information as to which geometric isomers were formed.

We believe that at present there is no satisfactory theory by which one can predict with assurance what isomer would be expected from the addition of bromine and chlorine to unsymmetrical butadienes. Ingold\(^6\) has applied, with a great deal of success, his theory to the addition reaction of diphenylbutadiene. On the basis of his theory he predicted that diphenylbutadiene would add chlorine predominantly in the 3,4- position. Straus\(^7\) had proven this years earlier. He also stated that 1-para-bromophenyl-4-phenylbutadiene would add bromine in the 3,4- positions. This has been found to be the case in these laboratories.\(^8\) On the basis of this observation one might expect that the substitution of a strongly meta directing group, such as the carboxyl group, for the ortho-para directing bromine atom in diphenylbutadiene might lead predominantly to the formation of the 1,4- and 1,2- isomers. Our experimental work clearly indicates that bromine adds predominantly to the 3,4 position of 1-p-carboxyphenyl-4-phenylbutadiene


\(^7\) Straus, *Ber.*, 42, 2872 (1901).

\(^8\) Huggins and Yokely, *J. Amer. Chem. Soc.*, 64, 1160 (1942).
just as it does to 1-p-bromophenyl-4-phenylbutadiene.
PART II

EXPERIMENTAL

Preparation of Cinnamyldene Acrylic Acid. 9—Ninety grams of cinnamaldehyde, 90 grams of malonic acid and 70 grams of pyridine were placed in a kjeldahl flask and refluxed on a water bath for eighteen hours.

\[
\begin{align*}
\text{H}_2\text{C} & \text{=C}\text{-C}=\text{O} + \text{H}_2\text{C} & \text{=C}\text{-OH} & \xrightarrow{\Delta} & \text{H}_2\text{C} \text{=C}\text{-C}=\text{O} \text{H}_2\text{N} \\
\end{align*}
\]

The brownish liquid was allowed to cool to room temperature, then poured slowly with stirring into a thirty per cent sulfuric acid ice mixture (150 grams of concentrated sulfuric acid, 350 grams of ice). The brownish yellow crystalline substance which separated was filtered.

The substance was dissolved in 500 ml. of acetic acid and allowed to stand overnight. The yellow crystalline substance which separated, was filtered and purified by recrystallization from benzene. The acid obtained melted at 164°-165°C. The yield was 62.3 g. (65.43%).

Preparation of \( \text{1,3-Phenylbutadiene} \).

\[9\] Doeber, J. Ber., 35, 2137 (1902).

\[10\] Ferguson, Marie, "The Preparation of 1,3-Carboxyphenyl 4-Phenylbutadiene-1,3" (Unpublished Master's thesis, Department of Chemistry, Atlanta University, 1941), p. 13.
The p-aminobenzoic acid was diazotized according to a method by Gilman.\textsuperscript{11}

\[
\begin{align*}
\text{HO}_2\text{C}-\text{NH}_2 + 2 \text{HCl} + \text{NaNO}_2 & \rightarrow \left[ \text{HO}_2\text{C}-\text{N}^=\text{N} \right] \text{Cl} + \text{NaCl} + 2 \text{H}_2\text{O} \\
\left[ \text{HO}_2\text{C}-\text{N}^=\text{N} \right] + 2 \text{H}^+ & \rightarrow \text{HO}_2\text{C}-\text{O}^+ + 2 \text{H}_2\text{O} + \text{N}_2 + \text{Cl}_2
\end{align*}
\]

P-Aminobenzoic acid (41.1 g), anhydrous sodium carbonate (42.9 g) and sodium nitrite (24 g) were dissolved in 600 ml. of water and the solution heated to boiling. After cooling to 0° C, the solution was added slowly and with stirring to a mixture of 300 ml. of concentrated hydrochloric acid and 300 g. of ice. After five minutes the diazo solution was added drop-wise to a cooled solution of 66 g. cinnamylidene acrylic acid dissolved in 1050 ml. of acetone with rapid stirring. Then cupric chloride (16.2 g.) and sodium acetate (82.5 g.), dissolved in 75 ml. of water were added. Nitrogen was evolved. The mixture was stirred for ninety minutes longer, allowing the temperature to rise to 15°, after which it was steam distilled until the distillate became clear. The non-volatile residue formed a black tar containing the desired compound and was filtered, while still hot, from the water solution.

The solid mass was allowed to cool then thoroughly

pulverized after which it was placed in benzene, heated to boiling and filtered while hot. The residue was dissolved in ethyl acetate, boiled and allowed to stand, whereupon crystals slowly settled out. These were filtered and recrystallized from additional ethyl acetate. Additional crystals were obtained by concentrating the ethyl acetate. The substance obtained gave a melting point of 252°C which corresponded to the melting point found in literature. A mixed melting point with the known compound gave no change in melting point. The yield was 5 g. (5.27%).

**Preparation of 1-p-Carboethoxyphenyl-4-Phenylbutadiene**

1,3. The preparation of 1-p-carboethoxyphenyl-4-phenylbutadiene 1,3 was carried out in a method analogous to the preparation of 1-p-carboxyphenyl-4-phenylbutadiene-1,3.\(^\text{10}\)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O}^\circ\text{L}-\text{N} \equiv \text{N}\text{H}_2 + 2\text{HCl} + \text{NaNO}_2 & \rightarrow \left[\text{C}_2\text{H}_5\text{O}^\circ\text{L}-\text{N} \equiv \text{N}\text{H}_2\right] \text{L} + \text{NaCl} + 2\text{H}_2\text{O} \\
\text{C}_2\text{H}_5\text{O}^\circ\text{L}-\text{N} \equiv \text{N}\text{H}_2 & \rightarrow \text{C}_2\text{H}_5\text{O}^\circ\text{L}-\text{N} \equiv \text{N}\text{H}_2 + \text{HCl} + \text{N}_2 + \text{CO}_2
\end{align*}
\]

Ethyl p-aminobenzoate (48.9 g.), anhydrous sodium carbonate (48 g.) and sodium nitrite (24 g.) were dissolved in 600 ml. of water and the mixture was added slowly with stirring to a mixture of 300 ml. of concentrated hydrochloric acid and 300 g.

---

of ice. After five minutes the diazo solution was added, dropwise with rapid stirring to a cooled solution of 60 g. cinnamylidene acrylic acid dissolved in 1050 ml. of acetone. Then cupric chloride (16.14) and sodium acetate (82.5 g.), dissolved in 75 ml. of water were added. Nitrogen was evolved. The mixture was stirred for ninety minutes longer allowing the temperature to rise to 15°C, after which it was steam distilled until the distillate became clear. The non-volatile residue formed a black tar containing the desired compound and was filtered, while still hot, from the water solution.

The solid mass was allowed to cool, then thoroughly pulverized; after which it was dissolved in ether. The ethereal solution was washed with twenty per cent sodium hydroxide, 20% hydrochloric acid and then water to remove all the unreacted cinnamylidene acrylic acid. When the solvent was removed a tarry mass was obtained which was purified by recrystallization with ethyl acetate. White crystals were obtained which gave a melting point of 125°-127°C. Yield 26.9 g. (29.52%).

Hydrolysis of 1-p-Carboethoxyphenyl-4-Phenylbutadiene.--- Into a 500 ml. round-bottomed flask fitted with a reflux condenser was placed 250 ml. of 10% potassium hydroxide and eight and a half grams of 1-p-carboethoxyphenyl-4-phenylbutadiene. This mixture was refluxed (steam cone) for one hour. On cooling white crystals settled out. The crystalline substance was dissolved in 200 ml. acetic acid and heated gently for one
half hour. On cooling yellow crystals settled out which were purified with ethyl acetate (m.p. 250°C); yield 4.5 g. (63.83%).

**Bromination of l-p-Carboxyphenyl-4-Phenylbutadiene-1,3.**—Three and eight tenth grams of l-p-carboxyphenyl-4-phenylbutadiene were dissolved in 150 ml. of ethyl acetate. Bromine (2.43 g. dissolved in 10 ml. of ethyl acetate) was then added drop-wise with constant shaking to the ethyl acetate solution of the diene. The solution was allowed to stand for four hours until decolorized. The solvent was concentrated to approximately 50 ml. under reduced pressure. The white crystals which separated gave a melting point of 176° - 177°.

**Analysis:** Calculated C_{17}H_{14}O_{2}Br_{2}: Br, 39.02%

Found: Br. 38.20%, 38.84%

**Attempted Reduction of l-p-Carboxyphenyl-4-Phenylbutadiene-1,3.**—To a 150 ml. round-bottomed flask fitted with a reflux condenser was added 3 g. of l p-carboxyphenyl 4-phenylbutadiene dissolved in 50 ml. of hot absolute ethanol. Three and three-tenth grams of sodium, cut into small pieces were added at such a rate that not more than three pieces were ever reacting in the flask. The flask was allowed to cool then the contents poured, with rapid stirring, into a 30% sulphuric acid ice mixture. The mixture was allowed to set overnight. The yellow crystalline material which separated after recrystallization with ethanol then ethyl acetate weighed 2.7 g. (90%). The crystals melted at 249°-250°C. and mixed melting
point determinations with the original 1-p-carboxyphenyl 4-phenylbutadiene 1,3 gave no change in melting point.

Ozonization of 1-p-Carboxylphenyl-3,4-Dibromo-Phenyl-butene.—Three and eight tenths grams of the dibromide were dissolved in 150 ml. of anhydrous ethyl acetate. The solution was cooled to 0°C and a stream of ozone passed through the solution for a period of six hours. The ethyl acetate was removed under reduced pressure. After the addition of twenty-five ml. of water the mixture was warmed (steam cone) for a period of two hours. The mixture was allowed to stand for twenty-four hours, then water was added to increase the volume to approximately 200 ml. The mixture was heated to boiling and filtered while hot.

The residue, α-β-dibromo β-phenyl propionic acid which weighed 1.14 g. (74%) was purified through recrystallization with fifty per cent methanol gave a melting point of 195°C (found in literature 195°C). The melting point did not change when a sample of this compound was mixed with authentic α-β-dibromo β-phenyl propionic acid. The amide was prepared which gave a melting point of 213°C-215°C (found in literature 217°C).

After concentrating the aqueous solution to approximately twenty-five ml. and allowing to cool, a white crystalline solid, terephthalic acid, which weighed 3.16 g. (79%) settled

13 Fock, Ber., 28, 2243 (1895).
out. Attempts to obtain a melting point of the material resulted in sublimation around 300°C.

The dimethyl ester\textsuperscript{14} of terephthalic acid was prepared which melted at 140°C-142°C, the melting point of Dimethyl Terephthalate. Mixed melting point determinations with authentic Dimethyl Terephthalate gave no change in melting point.

**The Preparation of 1,2-Dihydroxy-3,4-Dibromo-\textsubscript{1,p}-Carboxylyphenyl-4-Phenylbutane.--(The use of per Acetic Acid)\textsuperscript{15}**

A mixture of 100 ml. of glacial acetic acid and 40 ml. of hydrogen peroxide (30%) was placed in an Erlemeyer flask and heated for one hour at a temperature of 75°C-80°C. The solution was allowed to cool to 25°C. The dibromide (2 g.) was added to the cooled solution. The mixture was allowed to set overnight, then extracted with three 50 ml. portions of ether. The ethereal solution was washed with a 5% solution of sodium bicarbonate to remove the acetic acid. The ether solution was dried over calcium chloride, then the ether was removed by distillation under reduced pressure. The brown colored glycol was obtained as a viscous oil. Yield: 2.2 g.

**Analysis:** Calculated C\textsubscript{17}H\textsubscript{16}O\textsubscript{2}Br\textsubscript{2} ; Br 36.04%

**Found:** 35.39%, 35.46%


\textsuperscript{15}Scanlan and Swern, \textit{J. Am. Chem. Soc.}, 62, 2305 (1940).
The Cleavage of 1,2-Dihydroxy-3,4 Dibromo-1-p-Carboxylphenyl 4-Phenylbutanone. 16—Two and two tenths grams of the glycol were dissolved in 75 ml. of glacial acetic acid. An excess of lead tetraacetate, dissolved in glacial acetic acid was added to the mixture. The contents of the flask were kept at a temperature of 60—65°C for three hours then allowed to set overnight at room temperature.

The excess of lead tetraacetate was destroyed by titrating with glycerine, using potassium iodide starch paper as an indicator. Fifty ml. of water were added to the mixture. The mixture was extracted with ether. The ethereal solution was washed with a 5% solution of sodium bicarbonate, then water, after which the ether was removed using reduced pressure. The residue was placed in 50 ml. of water. Five ml. of hydrogen peroxide (30%) were added to the mixture and allowed to stand overnight. Extractions, using three 75 ml. portions of chloroform were made. The chloroform was removed from the chloroform extract using reduced pressure. The residue which weighed 0.7510 g. (84%) was purified through recrystallization with fifty per cent acqueous ethanol. Attempts to obtain a melting point resulted in sublimation around 300°C. The dimethyl ester was prepared which on purifying and drying melted at 140°-142°C; the melting point of Dimethyl Terephthalate. Mixed melting point determinations of the dimethyl ester with

dimethyl ester prepared from authentic Terephthalic acid gave no change in melting point.

The acqueous solution was concentrated to approximately 25 ml. On cooling and making the solution acidic, white crystals weighing 1.372 g. (88%) settled out which melted at 195°C the melting point of α-β-dibromo β-phenyl propionic acid. The amide was prepared which gave a melting point of 213°-215°C (found in literature 217°C.)

Preparation of 1,2,3,4-Tetrabromo-1-p-Carboxylphenyl 4-Phenylbutane.—One gram of 1-p-Carboxylphenyl-4-phenylbutadiene was dissolved in 75 ml. of ethyl acetate. An excess of bromine (1.6 g. dissolved in ethyl acetate) was added drop-wise with stirring. The white crystalline tetrabromide (m.p. 273°) settled out on setting overnight.

Analysis: Calculated C_{17}H_{14}O_{2}Br_{4}; Br 56.14%  
Found: 56.04%, 55.96%
PART III

SUMMARY

1. The hydrolysis of 1-p-Carboxoxyphenyl-4-Phenylbutadiene 1,3 gives better yields of 1-p-Carboxoxyphenyl-4-Phenylbutadiene-1,3 than the preparation through the coupling of p-amino benzoic acid and cinnamylidene acrylic acid.

2. The dibromination of 1-p-Carboxoxyphenyl-4-Phenylbutadiene 1,3 yields the 3,4- addition product in approximately 80 per cent theoretical yield.

3. The formation of the alcohol insoluble sodium salt of 1-p-Carboxoxyphenyl-4-Phenylbutadiene-1,3 does not allow the reduction of the alcohol soluble diene.
BIBLIOGRAPHY

Books


Articles


Huggins, K. A., and Yokely, O. E. "Studies on Substituted Diphenylbutadienes I. The Addition of Bromine to


Muskat, Irving E., Becker, B. C., and Lowenstein, J. S.


Unpublished Material

