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# Studies in conjugated systems: the reaction of 3-methyl-4-phenylbutadiene-1,3 with bromine

Simon A. Wicks  
*Atlanta University*

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STUDIES IN CONJUGATED SYSTEMS: THE REACTION OF  
3-METHYL-4-PHENYLBUTADIENE-1,3 WITH BROMINE

A THESIS

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

BY

SIMON A. WICKS

DEPARTMENT OF CHEMISTRY

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## CHAPTER I

### THEORETICAL

A large number of conjugated diene compounds and their halogenated products have been investigated with regard to preparation, structure and reaction mechanism.

The most important diene compound with a conjugated system is the 1,3-butadiene which is the chief constituent in synthetic rubbers.<sup>1</sup> Butadiene copolymerized with acrylonitrile gives a synthetic elastomer which is very resistant to attack by organic solvents. A liquid polymer of butadiene is used in varnishes, as a liner for food containers, in high temperature coatings, as a modifying agent for drying oils and alkyd resins.

This study is an investigation of the structure of the product formed by the reaction of bromine with 3-methyl-4-phenylbutadiene-1,3. The 3-methyl-4-phenylbutadiene-1,3 was prepared in 1944 by Kharasch<sup>2</sup> and again in 1956 by Alder.<sup>3</sup> The

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<sup>1</sup> Melvin J. Astle, "The Chemistry of Petrochemicals," the Reinhold Publishing Corporation, New York, 1956, p. 118.

<sup>2</sup> M. S. Kharasch, W. Nudenberg and E. K. Fields, J. Am. Chem. Soc., 66, 1279 (1944).

<sup>3</sup> Alder, Hayden, Heimback and Neufang, Ann., 586, 122 (1954).

reports read by the writer did not indicate that the above product had been brominated or treated with other halogen compounds.

The first method used on a large scale for the production of butadiene was that of ethyl alcohol.<sup>4</sup> The process was developed in Russia as a one-step vapor phase process. Ethyl alcohol vapors were passed over a catalyst consisting of aluminum oxide and zinc oxide at 400°C. and at a pressure of 0.25 atmosphere. This catalyst caused a simultaneous dehydrogenation and dehydration.



This process gave 60% butadiene based on the amount of alcohol.

A process developed by Carbide and Carbon Chemical Company consists of two steps.<sup>5</sup> The first step involves the dehydrogenation of ethyl alcohol to acetaldehyde and the second reaction is between acetaldehyde and ethyl alcohol.



Ethyl alcohol (95%) was vaporized and passed over a copper catalyst at about 400°C. to give acetaldehyde in about 92% yield. The aldehyde was then mixed with an excess amount of alcohol in a ratio of 3 moles of alcohol to 1 mole of aldehyde and passed

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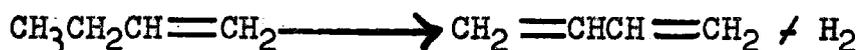
Melvin J. Astle, op. cit., p. 118.

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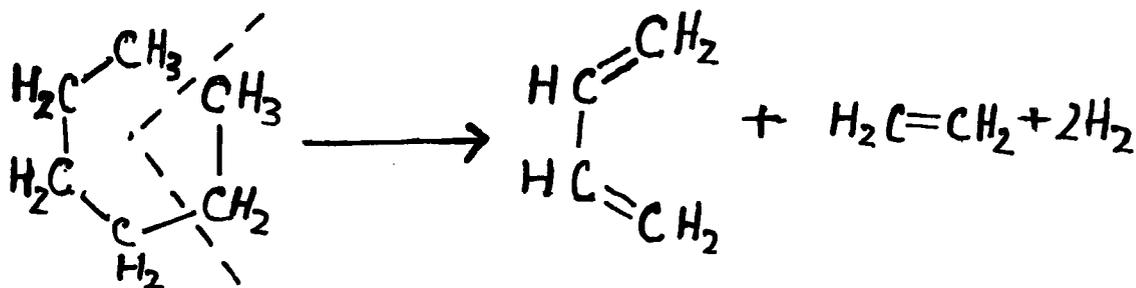
Melvin J. Astle, op. cit., p. 120.

over a tantala-silica catalyst (about 2% tantalum pentoxide on silica gel) at 325-350°C. The total yield of butadiene was 70% based on the amount of alcohol.

A more economical route to butadiene is the preparation from petroleum.<sup>6</sup> The cracking of liquid hydrocarbons at high temperatures (above 600°C.) using short reaction time always results in the formation of some butadiene. Short contact time is necessary to prevent further breakdown of butadiene or cyclization to form aromatic hydrocarbons. Egloff and Hulla noticed that there seemed to be a special tendency for butadiene to be formed from hydrocarbons having an even number of carbon atoms. Cleavage of the carbon chain may occur to give ethylene, which can subsequently polymerize to butenes, and then be dehydrogenated to butadiene.

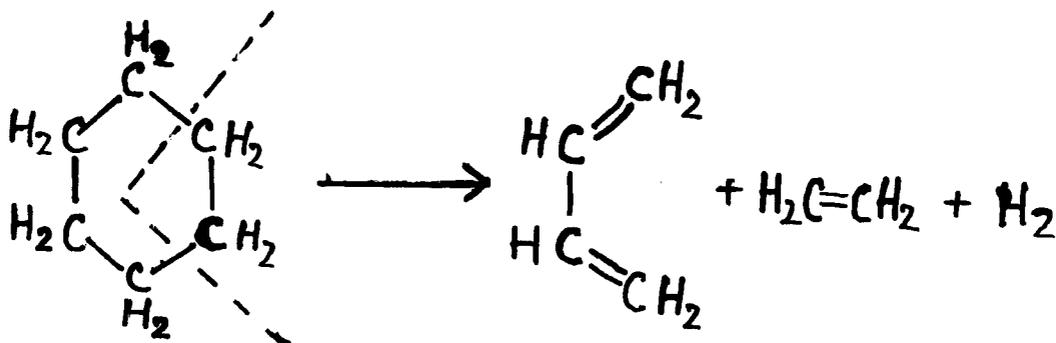


n-Hexane and cyclohexane may be cracked to give a mixture of butadiene, ethylene and hydrogen.



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Melvin J. Astle, op. cit., pp. 118-119.



All of these reactions have been observed.

Most of the butadienes are obtained by the catalytic dehydrogenation of n-butylenes. The butylenes in turn are obtained from the cracking of higher molecular weight hydrocarbons or by the dehydrogenation of n-butane.

Many dehydrogenation catalysts were investigated by the Rubber Reserve research program and those found most successful contained ferric oxide as the active ingredient. The most widely used catalyst contained 72.4% MgO, 18.4% Fe<sub>2</sub>O<sub>3</sub>, 4.6% K<sub>2</sub>O. Under normal conditions this catalyst had a life span of two to three months without regeneration. Other catalysts used consisted of chromic oxide and alumina. A recent catalyst developed by Phillips Petroleum Company for the dehydrogenation of butane contains 40% Cr<sub>2</sub>O<sub>3</sub> and 60% Al<sub>2</sub>O<sub>3</sub>.

There are several reactions of butadiene with halogens.<sup>7</sup> The reaction of butadiene with chlorine at low temperature gives two isomers, 1,4-dichloro-2-butene and 3,4-dichlorobutene-1, of

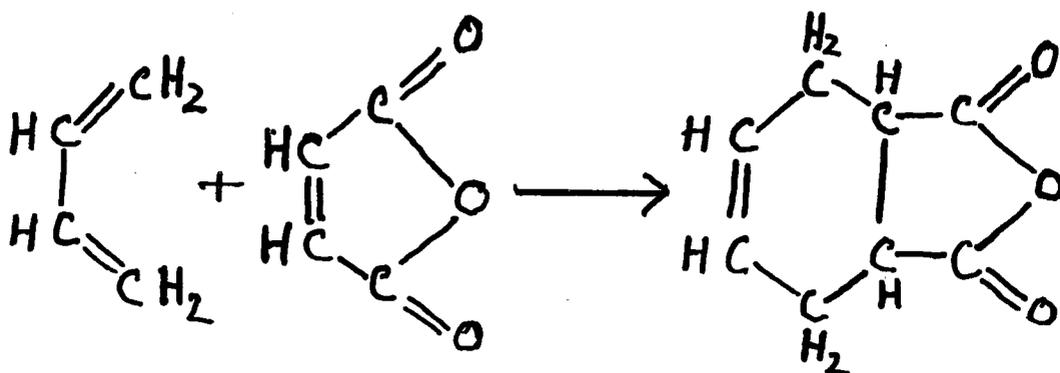
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<sup>7</sup> Melvin J. Astle, op. cit., p. 122.

which the 1,4-dichloride predominates. Mahler chlorinated butadiene in the absence of a solvent at 79°C. which gave a mixture of 3,4 and 1,4 dichlorobutenes in a ratio of 1 to 1.27 respectively.

Hilyer and Ice brominated butadiene in various solvents at a -20°C. The ratio of 1,2 to 1,4 dibromides in solvents such as hexane, chloroform and acetic acid was about the same as 46 to 54. In methyl cyclopentane, the ratio was reported to be 53 to 47.

The Diels-Alder reaction<sup>8</sup> consists of the 1,4 addition of an alkene or acetylenic linkage to a conjugated diene system.<sup>9</sup> The alkene or acetylenic compound which adds to the diene is referred to as the dienophile. An example is the reaction of butadiene with maleic anhydride to give tetrahydrophthalic anhydride.




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<sup>8</sup> E. Earl Royals, "Advanced Organic Chemistry," the Prentice-Hall, Inc., Englewood Cliffs, 1956, pp. 407-409.

<sup>9</sup> Ibid., p. 209.

The dienophile is a substance containing a carbon to carbon double or triple bond conjugated with an electron acceptor and exhibiting electrophillic reactivity on carbon. The reaction frequently gives high yields, permitting the synthesis of compounds that would be otherwise difficult to prepare. The method is limited to the formation of six-membered rings. There are a few limitations based on the nature of aromatic dienes which may be used in a Diels-Alder reaction. The reaction is fairly general for conjugated diene structures although some conjugated dienes have failed to react with maleic anhydride. But a positive reaction can be taken as proof of a conjugated diene structure.

The Diels-Alder reaction is characterized by extreme rapidity. In most cases the reaction occurs spontaneously on mixing the reactants with the evolution of heat. Solvents such as benzene, ether, or acetone are frequently used to effect a homogeneous reaction or to moderate a vigorous reaction. Normally no catalyst is used for the reaction, although trichloroacetic acid, trimethylamine, 1-napthoquinone have been reported to exert a catalytic effect. The Diels-Alder reaction is reversible and in many instances it can be used to purify conjugated dienes.

The addition of halogen to conjugated aliphatic substituted butadienes usually results in the 1,4 addition.<sup>10</sup> The following

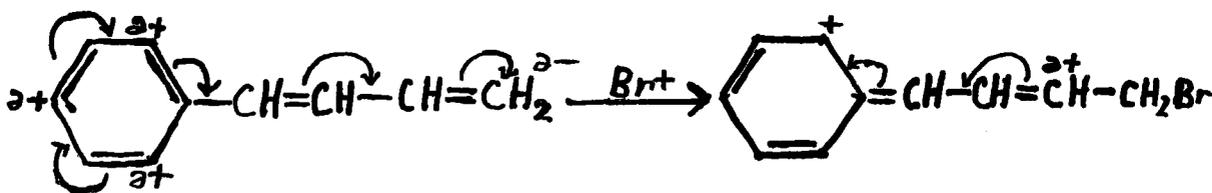
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<sup>10</sup>

Ibid., p. 402.

compounds have been reported to give mainly 1,4 addition on halogenation; isoprene,<sup>11</sup> 2,3-dimethylbutadiene,<sup>12</sup> 1,4-dimethylbutadiene,<sup>13</sup> and 2,3-di-t-butylbutadiene.<sup>14</sup> When 1,4-diphenylbutadiene is treated with bromine, the bromine adds in the 1,2 position.<sup>15</sup> According to Straus, the probable driving force which leads to the 1,2 rather than the 1,4 addition is the tendency of the remaining double bond of the product to be in conjugation with aromatic ring. The 1,4 addition would lead to an isolated double bond without being conjugated to either of the phenyl groups.

A more interesting example is that of Muskat and Huggins.<sup>16</sup> They brominated 1-phenylbutadiene, in which 1 mole of bromine was added to the 3,4 double bond.




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Jones and Williams, J. Chem. Soc., 829 (1934).

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Kondakow, J. prakt. Chem., 62, 166 (1900).

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Farmer, Lawrence, and Scott, J. Chem. Soc., 510 (1930).

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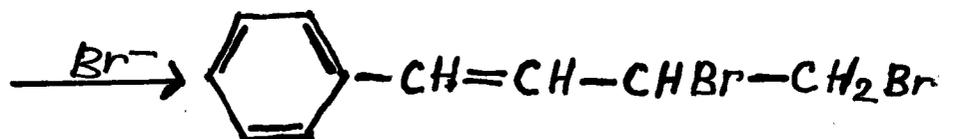
Backer, Rec. trav. chim., 58, 643 (1939).

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Straus, Ber., 42, 2867 (1909).

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Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

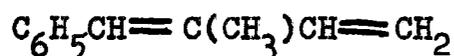
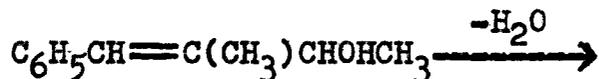
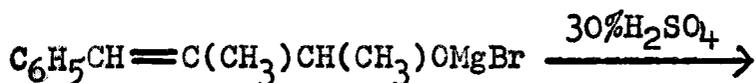
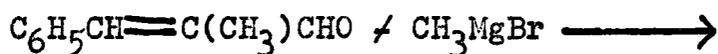
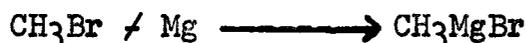


They describe the reaction according to the following procedure: The reaction is initiated by attack of positive bromine, and the entire unsaturated system including the benzene ring is utilized in supplying electrons to the attacking electrophilic reagent. The above mechanism accounts for the attack of positive bromine at carbon atom number four. The positive carbonium ion reacts with negative bromine by virtue of the partial positivity of carbon atom number three. According to their interpretation, 3,4 addition permits utilization of the entire conjugated system in supplying electrons for the initial attack. Retention of resonance energy of the benzene ring leaves the double bond in conjugation with the benzene ring.

## CHAPTER II

### EXPERIMENTAL PROCEDURE

Preparation of 3-Methyl-4-Phenylbutadiene-1,3.—To a 2-liter three neck glass ground joint flask fitted with condenser, dropping funnel and mechanical stirrer was added 24 g. of dry magnesium in 25 cc. of dry ethyl ether. To this mixture 100 g. of methylbromide in 100 cc. of dry ether was added dropwise with mechanical stirring. The reaction was controlled by cooling the reaction flask from the top. The reaction is exothermic and might cause the expulsion of ether from the reaction flask in forming the Grignard's reagent. After the reaction had subsided, 80 g. of alpha methylcinnamaldehyde in 150 cc. of dry ether was added dropwise with mechanical stirring. Equations for the reaction are as follows:



The reaction mixture was allowed to stand over night and then hydrolyzed and dehydrated according to the method of I. E.

Muskat and K. A. Huggins.<sup>17</sup> This process involves pouring the reaction mixture over a 30% sulfuric acid solution. The acid solution is prepared just before use, by mixing 150 g. (81.6 cc.) of sulfuric acid with 350 g. of ice. On pouring the reaction mixture into the acid solution, the mixture is stirred with a glass rod. The alkoxide magnesium bromide is hydrolyzed and dehydrated in the acid solution. The diene was taken up in the ether layer, in which the layer was dried over anhydrous sodium sulfate. Then the ether layer was placed in a vacuum desiccator and the ether was removed from the diene by suction with a water pump.

The diene was distilled in the following manner: To a 250 ml. Claisen flask, a small amount of hydroquinone was added to curb polymerization during the distillation process. A small amount of anhydrous  $\text{KHSO}_4$  and anhydrous  $\text{Na}_2\text{SO}_4$  was added to remove the last trace of water. Then 71.5 cc. of the diene was added and distilled at reduced pressure. The fraction boiling between  $78-90^\circ\text{C}$ . at 0.5 mm. of pressure was collected. The diene was redistilled, collecting the fraction boiling between  $78-85^\circ\text{C}$ . at 0.5 mm. of pressure. The crude yield was 67%.

The Bromination of 3-Methyl-4-Phenylbutadiene-1,3.—In a 500 ml. three neck ground joint flask, fitted with a mechanical stirrer, dropping funnel, and condenser, 37.4 g. of the diene

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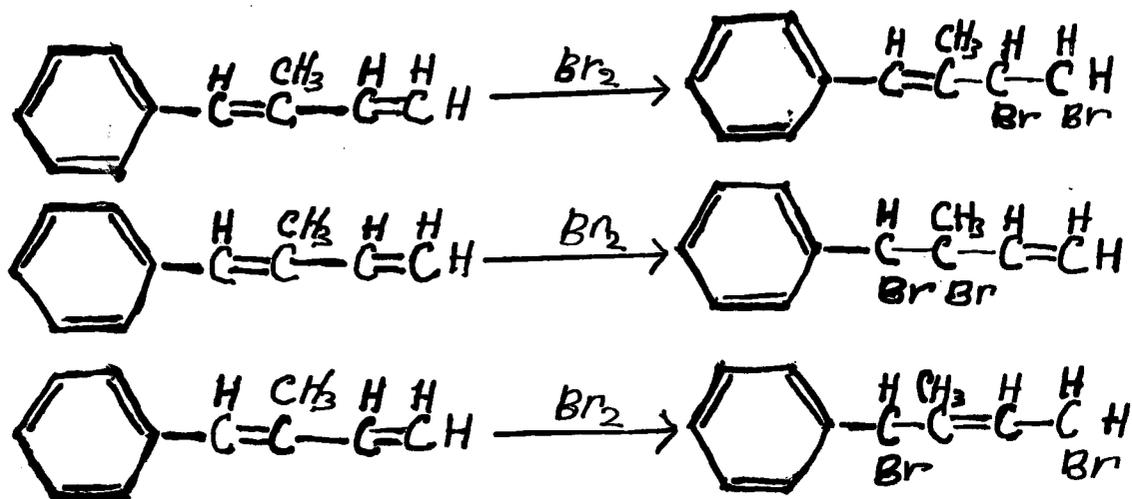
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I. E. Muskat and K. A. Huggins, J. Am. Chem. Soc., 51 2996 (1929).

in 100 ml. of  $\text{CCl}_4$  was added. The flask was cooled to  $0^\circ\text{C}$ . with a salt ice bath. Then 41.5 g. (14.17 cc.) of bromine in 85 ml. of  $\text{CCl}_4$  was added dropwise with mechanical stirring. Time of addition was 3 hours, and stirring continued for 8 hours. The reaction mixture was placed in a vacuum desiccator and the  $\text{CCl}_4$  was removed by suction with a water pump. The product formed by the bromination of the diene was distilled from a 250 ml. Claisen flask under reduced pressure. The fraction distilling between  $125\text{--}135^\circ\text{C}$ . at 0.5 mm. of pressure was collected. The yield was 76%. The product was a yellowish-green oil which turned dark on standing.

Anal. Calcd. for  $\text{C}_{11}\text{H}_{12}\text{Br}_2$ : C, 43.42; H, 3.98; Br, 52.60.  
Found: C, 43.79; H, 4.08; Br, 52.50.

The theoretical products for the brominated diene are as follows:



Ozonolysis.—Eleven grams of 3-methyl-4-phenyldibromobutene

in 125 cc. of dichloromethane was ozonized by passing ozone through the solution for three hours. The solution was cooled to 0°C. during the ozonolysis process. The complete ozonolysis of the alkene was indicated by the action of ozone on a solution of potassium iodide and starch, which gave a dark blue color. The solvent was removed with a water pump, and the ozonide was hydrolyzed with 50 cc. of water. Upon steam distillation of the hydrolysis products, a pale yellow oil came over with the distillate which gave a positive Schiff test and reacted with 2,4-dinitrophenylhydrazine, prepared according to Brady's Method<sup>18</sup> to form a yellow crystalline solid. When the solid was recrystallized with ethyl alcohol, it gave a negative halogen test and a melting point of 236-237°C. This melting point corresponded with that of 2,4-dinitrophenylhydrazone derivative of benzaldehyde, m. p. 236°C. When a mixed melting point of these derivatives was taken no change in melting point resulted.

Anal. Calcd. for  $C_{13}H_{10}N_4O_4$ : C, 54.54; H, 3.49; N, 19.58.  
Found: C, 54.91; H, 3.72; N, 19.06.

The residue from the steam distillation process contained a brownish oil which seemed to have reacted with 2,4-dinitrophenylhydrazine, but no crystals were formed. It gave a negative Schiff test and was taken to be 1,2-dibromoethyl methyl ketone. This compound was prepared by Schlotterberg,<sup>19</sup>

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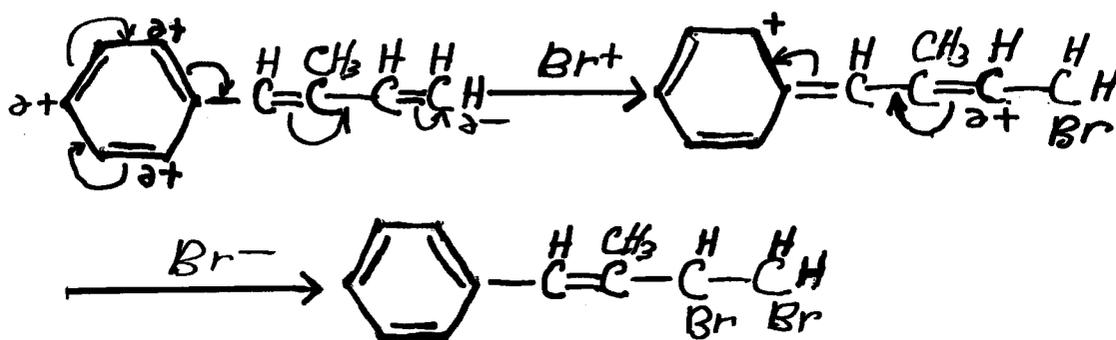
<sup>18</sup> J. Brady, The Chem. Soc., 757 (1931).

<sup>19</sup> Schlotterberg, Ber., 42, 2563 (1909).

but no derivatives were reported.

When the brominated product was treated with a solution of potassium iodide in acetone, bromine was removed indicating that the bromine atoms were on adjacent carbon atoms. The product formed by the bromination of 3-methyl-4-phenylbutadiene-1,3 is taken to be 1,2-dibromo-3-methyl-4-phenylbutene-3, a 1,2 addition product. From the theoretical structures of 3-methyl-4-phenyl-dibromobutene only the above structure could have the bromine atoms on adjacent carbon atoms and give rise to benzaldehyde on ozonolysis. An attempted chromatographic separation of the 2,4-dinitrophenylhydrazone precipitate indicated only the derivative of benzaldehyde.

The addition of bromine to 3-methyl-4-phenylbutadiene-1,3 is considered to be in keeping with that described by Muskat and Huggins on page seven of this paper. An equation for the reaction is interpreted as follows:



The 1,2 addition leaves the double bond in conjugation with the benzene ring which is favored over that of an isolated double



In the periodic acid oxidation of 3-methyl-4-phenyldibromobutene, no initial oxidation products were isolated in sufficient quantities to verify a definite structure. This procedure is not considered to be a good one, due to the presence of iodine from the periodic acid in the solution, which caused some of the test results to be misleading. The 2,4-dinitrophenylhydrazone derivative of the condensation product was formed in fair quantity and purified.

Similar results were obtained when the brominated product was hydroxylated according to that described by Daniel,<sup>20</sup> followed by cleavage with periodic acid.

To a well stirred solution of 7.4 g. of phenyldibromobutene in 42.3 ml. of formic acid, 6.9 g. of 25% hydrogen peroxide was added in one portion. The temperature was maintained at 40°C. for two hours at which time the mixture was diluted with cold water and treated with periodic acid. After the mixture had stood for ten hours, it was extracted with ether. The ether was removed with a water vacuum pump and a dark oil was left as a residue. This residue reacted with 2,4-dinitrophenylhydrazine to give a yellowish crystalline solid, m. p. 170°C. The solid gave a positive halogen test and is believed to be the same as the crystals formed by the reaction of 2,4-dinitrophenylhydrazine with the periodic acid oxidation product of phenyldibromobutene

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Swern Daniel, Geraldine N. Billen, Thomas W. Findley and John T. Scanlan, J. Am. Chem. Soc., 67, 1787 (1945).

which melted at 168°C.

Analysis of the product melting at 168°C. suggested that condensation occurred between the initial oxidation products of phenyldibromobutene.

## CHAPTER III

### SUMMARY

The study of the reaction of bromine with 3-methyl-4-phenylbutadiene-1,3 revealed that 1,2 addition is the predominant reaction. The 1,2 addition product was supported by the isolation of benzaldehyde on ozonolysis through its 2,4-dinitrophenylhydrazone derivative and the removal of bromine from 3-methyl-4-phenyldibromobutene with a solution of potassium iodide in acetone, which would occur only if the bromine atoms were on adjacent carbon atoms.

The oxidative cleavage of 3-methyl-4-phenyldibromobutene was substantiated by the analysis of 2,4-dinitrophenylhydrazone of a condensation product, which corresponded molecularly to a product formed by the condensation of benzaldehyde with 1,2-dibromoethyl methyl ketone.

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