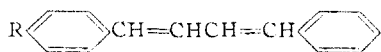


[CONTRIBUTION FROM THE ATLANTA UNIVERSITY CHEMICAL LABORATORY]

Studies on Substituted Diphenylbutadienes. I. The Addition of Bromine to 1-*p*-Bromophenyl-4-phenyl-1,3-butadiene

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In a general study of the mode of addition of halogens and hydrogen halides to some diphenylbutadienes of the type



where R— is bromine, chlorine or a radical containing unshared electrons capable of forming a resonating system with the benzene ring, the action of bromine on 1-*p*-bromophenyl-4-phenyl-1,3-butadiene has been examined. According to the theory of Ingold,¹ the addition should take place almost exclusively in the 3,4-positions. The present investigation has shown this to be the case.

1-*p*-Bromophenyl-4-phenylbutadiene was prepared according to the method used by Kuhn and Winterstein² in the synthesis of diphenylbutadiene. The structure of the *p*-bromophenyl-4-phenylbutadiene was established by its ready condensation with maleic anhydride and its addition of four atoms of bromine.

The bromination of 1-*p*-bromophenyl-4-phenylbutadiene was studied. It was found that this compound readily absorbs two atoms of bromine to form a crystalline dibromide, the structure of which was determined by ozonolysis and by oxidation with potassium permanganate in acetone solution. Three dibromides are theoretically possible depending on whether 1,2-, 1,4- or 3,4-addition takes place. It was possible to isolate from the ozonization products a 64% yield of α,β -dibromohydrocinnamic acid and a 62% yield of *p*-bromobenzaldehyde calculated from the semicarbazone and the *p*-benzoic acid isolated.

In some experiments ozonization was carried out at temperatures of an ice-salt bath with dibromide which had not been isolated from the chloroform in which it was formed. This was done to avoid heating which might cause the less stable dibromides to rearrange. However, in no case were we able to isolate any of the products to be expected from either the 1,2- or 1,4-isomers. Oxidation with potassium permanganate yielded similar results. This is conclusive evidence that bromine adds to 1-*p*-bromophenyl-4-phenylbutadiene almost exclusively in the 3,4-positions.

¹ Ingold, *J. Chem. Soc.*, 2354 (1931).

² Kuhn and Winterstein, *Ann. Chem. Phys.*, 11, 119 (1925).

Experimental

1-*p*-Bromophenyl-4-phenyl-1,3-butadiene.—A mixture of *p*-bromophenylacetic acid (63 g.), dry lead monoxide (39.12 g.), freshly distilled cinnamic aldehyde (38.6 g.), and purified acetic anhydride (57.27 g.) was heated for five hours and allowed to stand overnight. The yellow semi-solid mass which separated was filtered with suction, washed with 95% alcohol, and crystallized from acetic acid and then from a mixture of benzene and alcohol. After three crystallizations from benzene and alcohol, the almost colorless crystals melted at 163°. The compound was soluble in benzene, ether, chloroform, but only slightly soluble in ligroin, and carbon tetrachloride. The yield calculated on the basis of the cinnamic aldehyde was 15.3 g or 18.4% of the theoretical.

Anal. Calcd. for C₁₆H₁₅Br: C, 67.39; H, 4.56; Br, 28.07. Found: C, 67.29; H, 4.73; Br, 27.95, 28.00.

Reaction of 1-*p*-Bromophenyl-4-phenylbutadiene with Maleic Anhydride.—A maleic anhydride derivative of *p*-bromophenyl-phenylbutadiene was prepared by refluxing equimolar quantities of the two compounds in dry thiophene-free benzene for eight hours. The solid crystallized from the cooled solution in 91% yield, as white needles, melting at 226°.

Anal. Calcd. for C₂₀H₁₅O₃Br: C, 62.67; H, 3.91. Found: C, 62.66; H, 3.96.

1-*p*-Bromophenyl-phenyltetrabromobutane.—A solution of 1-*p*-bromophenyl-phenylbutadiene dissolved in 40 ml. of chloroform was cooled to 0° and treated dropwise, with vigorous shaking, with a slight excess of bromine in the same solvent. In a short while a white, finely divided precipitate separated. After standing overnight the solvent was removed under diminished pressure and the residue crystallized from a mixture of benzene and ligroin. A recrystallized sample melted at 230°. Analysis for bromine indicated that the compound was a tetrabromide of *p*-bromophenyl-phenylbutadiene.

Anal. Calcd. for C₁₅H₁₃Br₅: Br, 67.6. Found: Br, 67.37.

The Dibromide of 1-*p*-Bromophenyl-4-phenylbutadiene.—1-*p*-Bromophenyl-4-phenylbutadiene (11.62 g.) was dissolved in freshly distilled chloroform and cooled to 0°. To this solution was added dropwise and with constant shaking a solution of bromine (7.52 g.) in 20 ml. of chloroform. The solvent was removed *in vacuo* at room temperature and the solid crystallized from ligroin. The product after purification by three recrystallizations from the same solvent melted at 129–130°. Analysis of the crystalline product for bromine indicated that the compound was a dibromide.

Anal. Calcd. for C₁₆H₁₃Br₂: Br, 53.93. Found: Br, 53.87, 53.92.

Ozonolysis of the Dibromide of 1-*p*-Bromophenyl-4-phenylbutadiene.—The ozonizer used was similar to the

one described by Henne.³ The dibromide (4.34 g.) was dissolved in carefully purified chloroform and a current of ozonized oxygen was bubbled through the cooled solution for twenty-four hours. A white crystalline solid which separated during ozonization was removed by filtration and a portion of the chloroform was removed under diminished pressure when a second crop of crystals separated. These crystals were removed by filtration, combined with those previously obtained and recrystallized from chloroform. The solid melted at 195°, the melting point of α,β -dibromohydrocinnamic acid. The melting point of a mixture of this solid with authentic α,β -dibromohydrocinnamic acid was 195°. The yield of this acid was 1.94 g. or 64.8% of the theoretical.

After removal of the remaining solvent under diminished pressure, the ozonide was decomposed according to the method used by Straus⁴ in working up the ozonide of the dibromide of diphenylbutadiene. The residue was treated with an alcoholic solution of potassium acetate and warmed under a reflux condenser for two hours. Water was added to the alcoholic solution consisting of aldehydes, bromostyrene, phenylacetylene and acids and the mixture was extracted several times with ether. The ethereal solution was washed with dilute sodium hydroxide, water, and dried. After removal of the ether the residue was treated with an aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to render the solution neutral. A semicarbazone (0.0360 g.) was precipitated after a short time. It was recrystallized several times from alcohol and melted at 227°, the melting point of the semicarbazone of *p*-bromobenzaldehyde. A mixture of the semicarbazone with a sample of known origin melted at the same temperature.

The combined alkaline extracts containing the acid fractions were acidified with dilute sulfuric acid. A white solid mostly *p*-bromobenzoic acid was precipitated. This solid was dissolved in a warm sodium hydroxide solution and reprecipitated with dilute sulfuric acid. After crystallization first from ligroin and hot water it melted at 252°, the melting point of *p*-bromobenzoic acid. A mixture with a sample of known *p*-bromobenzoic acid also melted at 252°. The combined yield of *p*-bromobenzoic acid and the semicarbazone of *p*-bromobenzaldehyde was 62.26%.

Oxidation of the Dibromide of 1-*p*-Bromophenyl-4-phenylbutadiene with Potassium Permanganate.—The procedure used in this experiment was similar to that described by Farmer and Scott.⁵ To an ice-cooled solution of the dibromide (2.136 g.) in 39.96 ml. of acetone was added an aqueous solution containing 2.04 g. of potassium permanganate and 2.04 g. of magnesium sulfate. This solution was added slowly and care was taken to see that the temperature did not rise above 0°. The reaction mixture was filtered and the acetone removed from the filtrate by a

rapid current of air. The mud was suspended in a little water and just brought into solution by means of sulfuric acid and sodium bisulfite. This solution after the removal of unchanged dibromide by filtration was combined with the acetone-free filtrate and extracted ten times with ether. The ethereal extracts were freed from any acids by cautious agitation with a solution of sodium bicarbonate and then dried over anhydrous sodium sulfate. After removal of the solvent, *p*-bromobenzaldehyde identified as its semicarbazone was isolated.

The alkaline filtrates containing the acid fragments were combined and acidified with dilute sulfuric acid and extracted with a large volume of ether. The ethereal solution was dried over sodium sulfate. After evaporation of the ether the residue was extracted with chloroform which removed the *p*-bromobenzoic acid. The α,β -dibromohydrocinnamic acid which is almost insoluble in chloroform remained on the paper when the solution was filtered and after recrystallization from chloroform melted at 195°. The melting point of a mixture of this acid with the authentic α,β -dibromohydrocinnamic acid was 195°. After removal of the chloroform the solid left in the flask was dissolved in sodium hydroxide and warmed for an hour. The alkaline solution was then extracted with ether to remove any bromostyrene or phenylacetylene that might have been formed by the decomposition of the α,β -dibromohydrocinnamic acid, and treated with dilute sulfuric acid. A white solid separated which after crystallization, first from ligroin, and finally from hot water, melted at 252°, the melting point of *p*-bromobenzoic acid. The melting point of a mixture of this acid and known *p*-bromobenzoic acid was the same. The isolation of *p*-bromobenzoic acid and α,β -dibromohydrocinnamic acid is conclusive evidence that the 1-*p*-bromophenyl-4-phenylbutadiene adds bromine in the 3,4 positions.

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Summary

1. The preparation of 1-*p*-bromophenyl-4-phenyl-1,3-butadiene has been described.
2. When 1-*p*-bromophenyl-4-phenylbutadiene was brominated a crystalline dibromide was formed whose structure was proved by ozonolysis to be a 3,4-derivative which is in accord with Ingold's theory of addition to conjugated systems.
3. The 3,4-dibromo-*p*-bromophenyl-4-phenylbutene was further brominated to give a tetrabromophenyl-phenylbutane.
4. 1-*p*-Bromophenyl-4-phenylbutadiene readily condensed with maleic anhydride.

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(3) Henne, *THIS JOURNAL*, **51**, 2676 (1929).

(4) Straus, *Ber.*, **42**, 2866 (1909).

(5) Farmer and Scott, *J. Chem. Soc.*, 172 (1929).