[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. XI. THE OXIDATION OF CIS-PHENYLBUTADIENE BY MEANS OF PERBENZOIC ACID[1]

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Perbenzoic and peracetic acids have been used for some time to determine the degree of unsaturation and the rate of oxidation of olefinic compounds.[2] Of particular interest in our investigations is the work of Böeseken and Blumberger on the three isomeric phenylbutenes, $\Delta^{1,2}$-$C_6H_5—CH{=}CH—CH_2—CH_3$; $\Delta^{2,3}$-$C_6H_5—CH_2—CH{=}CH—CH_3$; $\Delta^{3,4}$-$C_6H_5—CH_2—CH_2—CH{=}CH_2$; and also on cinnamic acid and its methyl ester.[3] In the case of the phenylbutenes they found that the nearer the double bond is to the phenyl group the greater is the rate of oxidation; while both cinnamic acid and its ester are insensitive to oxidation by means of perbenzoic acid. From these facts they concluded that the phenyl group hastens the oxidation while the carboxyl group, at least when it is situated next to the double bond, hinders oxidation by means of perbenzoic acid.

Meerwein[4] has reported results similar to those on the phenylbutenes, from his study of the rate[5] of oxidation of safrole, isosafrole, eugenol and isoeugenol.

Arbuzov and Mikhailow[6] have studied the oxidation of unsaturated compounds by means of peracetic and perbenzoic acids and from their work have concluded that the first step in the oxidation reaction is the formation of cyclic oxides. Böeseken and his collaborators[7] recently have accepted this view although they had previously assumed that peracetic acid is absorbed by the double bond to give the monoacetate of the diol while perbenzoic acid oxidized the double bond directly to the cyclic oxide.

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[1] Presented before the Organic Division of the American Chemical Society at its meeting in Buffalo, N. Y., 1931.

[2] Prileschajew, *Ber.*, **42**, 4811 (1909); *J. Russ. Phys.-Chem. Soc.*, **42**, 1387 (1910); **43**, 609 (1911); **44**, 613 (1912). For later work on detection and quantitative determination of unsaturation, see Bauer and Kutscher, *Chem. Umschau*, **32**, 57 (1925); Nametkin, *J. prakt. Chem.*, **112**, 169 (1926); *ibid.*, **115**, 56 (1927); Pummerer, *Ber.*, **62**, 1411 (1929); **62**, 2636 (1929); Smit, *Rec. trav. chim.*, **49**, 675 (1930); *ibid.*, **49**, 691 (1930). Derx, *ibid.*, **41**, 332 (1922).

[3] Böeseken and Blumberger, *ibid.*, **44**, 90 (1925); **45**, 838 (1926).

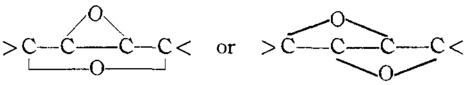
[4] Meerwein and co-workers, *J. prakt. Chem.*, **113**, 9 (1926).

[5] For work on velocities of oxidation by means of peracetic acid, see Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1928); Smit, *Rec. trav. chim.*, **49**, 686 (1930).

[6] Arbuzov and Mikhailow, *J. prakt. Chem.*, **127**, 1 (1930); *ibid.*, **127**, 92 (1930).

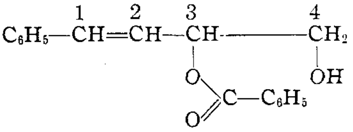
[7] Böeseken, *ibid.*, **131** (ii), 285 (1931).

Several authors[8] have studied the oxidation of unsaturated fatty acids and their esters by means of both peracetic and perbenzoic acids. It has been found that in the case of compounds containing two double bonds, whether conjugated or not, a dioxide is formed. Smit[8] found that in the case of 9,12-linolic acid the dioxide that is formed can be hydrolyzed but in the case of the conjugated 9,11-linolic acid the dioxide cannot be hydrolyzed. He suggests, therefore, these two possible structures for the dioxide of the conjugated compound.



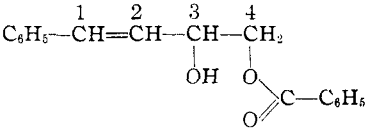
In our work on the oxidation of *cis*-phenylbutadiene by means of perbenzoic acid, we have found that the products obtained depend largely on the temperature at which the reaction takes place. At 0° only one double bond of the unsaturated compound is attacked, while at 25° both double bonds are attacked.

If equimolar quantities of *cis*-phenylbutadiene and perbenzoic acid in chloroform solution are allowed to react at 0°, a white crystalline compound, m. p. 81–82°, is formed. This compound was proved by analysis to be an hydroxybenzoate formed by the addition of a mole of perbenzoic acid to one of the double bonds. The position of the remaining double bond was established by the isolation of the semicarbazone of benzaldehyde on ozonization. This proves, therefore, that the perbenzoic acid is absorbed in the 3,4-positions of phenylbutadiene and the benzoate must have one of the structures



I

or



II

No effort was made to distinguish between these two possible structures, but on the basis of previous work[9] on the addition reactions of phenylbutadiene, and on the basis of the chemical reactions of the benzoate, which are to follow, structure I is favored.

The fact that the double bond farther removed from the phenyl group is attacked more readily than is the one next to the phenyl group is in agreement with the previous work of Muskat and co-workers[9] but contrary to the conclusions drawn by Böeseken[3] and Meerwein.[4] Also,

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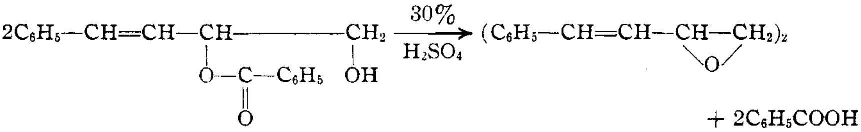
[8] Bauer and Kutscher, *Chem. Umschau*, **325,** 57 (1925); *J. prakt. Chem.*, **122,** 201 (1929); Böeseken, *Chem. Abs.*, **23,** 4192 (1929); *Rec. trav. chim.*, **49,** 91 (1930); Smit, *ibid.*, **49,** 675 (1930); Braun, THIS JOURNAL, **52,** 3188 (1930).

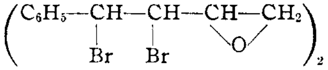
[9] Muskat and Huggins, *ibid.*, **51,** 2496 (1929); Muskat and Grimsley, *ibid.*, **52,** 1574 (1930).

the fact that a hydroxybenzoate was isolated as the *primary oxidation product* indicates that oxidation by means of perbenzoic acid occurs by the preliminary absorption of the peracid by the unsaturated compound, rather than through the formation of cyclic oxides as is postulated by Böeseken[7] and Arbuzov.[6]

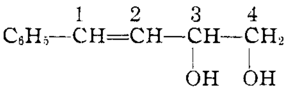
The benzoate was warmed on the steam-bath for twenty-four hours with 30% sulfuric acid. A white solid, m. p. 192°, and benzoic acid were isolated. The white solid, m. p. 192°, was found to be a dimer of phenylbutadiene monoxide. The position of the double bond was established by the isolation of benzoic acid on ozonization.



The fact that the double bond is not involved in the polymerization was established by the amount of benzoic acid isolated from ozonization—80% calculated on the basis of two moles of benzoic acid per mole of dimer—and confirmed by bromination. One mole of the dimer of phenylbutadiene monoxide absorbed two moles of bromine to give the tetrabromide of the dimer, m. p. 220°.

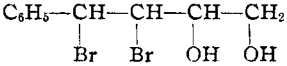


When the benzoate was treated with dilute sodium hydroxide solution at room temperature or even at 0°, it was hydrolyzed to a dihydroxy derivative of phenylbutadiene, a white crystalline material, m. p. 74°. When ozonized, the dihydroxy derivative yielded benzaldehyde, which proved the 3,4-structure of the dihydroxy derivative.



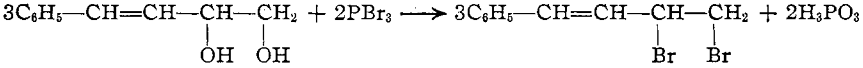
$$C_6H_5-\overset{1}{CH}=\overset{2}{CH}-\underset{OH}{\overset{3}{CH}}-\underset{OH}{\overset{4}{CH_2}}$$

The dihydroxy derivative was dehydrated by means of phosphorus pentoxide in anhydrous ether solution and also by heating with 30% sulfuric acid in a bomb tube. The product obtained in each case was the dimer of phenylbutadiene monoxide, m. p. 192°. The dihydroxy derivative absorbed bromine to form 1,2-dibromo-3,4-dihydroxy-1-phenylbutane, m. p. 94°.



$$C_6H_5-\underset{Br}{CH}-\underset{Br}{CH}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

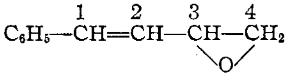
In order to link the work on oxidation with that on other addition reactions of conjugated compounds,[9] the dihydroxy derivative was treated with phosphorus tribromide in anhydrous ether solution. The known 3,4-dibromide of phenylbutadiene, m. p. 94°, was obtained.



$$3C_6H_5\text{—}CH{=}CH\text{—}\underset{OH}{CH}\text{—}\underset{OH}{CH_2} + 2PBr_3 \longrightarrow 3C_6H_5\text{—}CH{=}CH\text{—}\underset{Br}{CH}\text{—}\underset{Br}{CH_2} + 2H_3PO_3$$

The tetrabromide of phenylbutadiene, m. p. 146°, was formed when the dihydroxy derivative of phenylbutadiene was treated with phosphorus pentabromide in anhydrous ether solution.

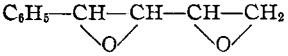
Accompanying the hydroxybenzoate there was always a small amount of the monoxide of phenylbutadiene, b. p. 88° under 1 mm. pressure. Again, the position of the double bond was determined by ozonization. Benzaldehyde was isolated as one of the ozonization products, which proved the 3,4-structure of the monoxide of phenylbutadiene.



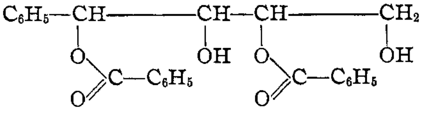
The monoxide yielded the dimer of phenylbutadiene monoxide when heated with 30% sulfuric acid on the steam-bath.

In addition to the small amounts of monoxide separated from the original reaction mixture, the monoxide has been obtained in very small amounts by heating the hydroxybenzoate at atmospheric pressure. Fifty per cent. of the theoretically possible yield of monoxide has been obtained by heating, in a bomb tube, the hydroxybenzoate in methyl alcohol solution containing a drop or two of dilute hydrochloric acid.

If two moles of perbenzoic acid are allowed to react with one mole of *cis*-phenylbutadiene at 25°, an oil is obtained from which two products were isolated: (1) an oil which distilled at 97° under 1 mm. pressure and was proved by analysis to be the dioxide of phenylbutadiene (A); and



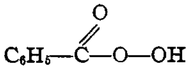
A



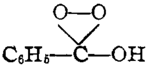
B

(2) a crystalline residue, m. p. 186°, which proved to be the dihydroxydibenzoate of phenylbutadiene. The most probable structure for this compound is (B).

From the work presented above it is quite evident that the structure of perbenzoic acid must be represented as

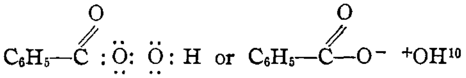


rather than

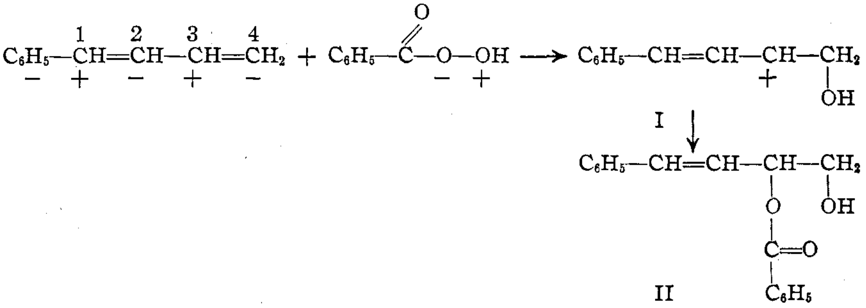


as was suggested by Böeseken

The electronic structure of perbenzoic acid would then be indicated as



In a recent paper, Muskat and Northrup[11] developed a rather comprehensive electronic theory of the addition reactions of conjugated systems, which affords an explanation of the apparent discrepancies in the mode of addition of various reagents to such systems. According to this theory, "The addition of both components of the addendum to an ethylenic double bond does not occur simultaneously. It is more likely, as has been suggested by Stieglitz,[12] that the essential feature is the attraction of the positive substituting group to the negative carbon valencies." It follows as a direct corollary to this theory that the addition of different reagents to a particular conjugated compound should be fundamentally the same. Since we have previously found that the halogens and hypohalous acids—oxidizing agents—are added to phenylbutadiene in the 3,4-positions, we should expect that perbenzoic acid would also be added to—oxidize—the 3,4-double bond. The mechanism of the addition would then be represented as[11]



In the first step of the reaction the positive hydroxyl group $\overset{+}{(OH)}$ is absorbed by the negative carbon atom (4) to give the intermediate I. The intermediate I would not undergo a 1,3-rearrangement to $C_6H_5—\underset{+}{CH}—CH=CH—CH_2OH$ due to the hindering influence of the phenyl group,[11] therefore the negative component, $C_6H_5—CO—O^-$, is absorbed by the 3-carbon atom to give hydroxybenzoate II. As has already been shown above, perbenzoic acid is actually absorbed by phenylbutadiene in the 3,4-positions to give the hydroxybenzoate II. At higher temperatures the 1,2-double bond is also attacked.

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[10] The + and − signs as used here do not represent a complete transfer of electrons, but simply indicate that the atoms so marked are relatively electropositive or electronegative with respect to the atoms marked oppositely. See discussion by Muskat and Stieglitz to be published soon.

[11] Muskat and Northrup, This Journal, **52**, 4043 (1930).

[12] Stieglitz, *ibid.*, **44**, 1304 (1922).

Experimental Part

Oxidation at Zero Degrees

Preparation of the Hydroxybenzoate of Phenylbutadiene.—A chloroform solution of perbenzoic acid was prepared by the method of Tiffeneau,[13] by treating benzoyl peroxide with sodium ethylate, liberating the perbenzoic acid with sulfuric acid and extracting with chloroform. The dried perbenzoic acid solution was cooled to 0° and slightly less than an equivalent amount of *cis*-phenylbutadiene was added, so that about a 2% excess of perbenzoic acid was present. The mixture was allowed to stand at 0° until oxidation was complete as indicated by iodimetric titration. The time required for this is about forty-eight hours. The chloroform was removed by means of suction without warming and the resulting pasty mass of crystals and oil was taken up in ether. The ether solution was shaken with iced 5% sodium hydroxide for half to three-quarters of an hour to remove the benzoic acid.[14] Care was taken to prevent heating and consequent increased hydrolysis when the alkali was added. The ether solution was separated, washed with water, dried over anhydrous sodium sulfate and filtered. The ether was removed by vaporization. A mass of flaky white crystals remained, which was recrystallized from hot low-boiling ligroin. The pure crystals melted at 81–82°.

Anal. Calcd. for $C_{17}H_{16}O_3$: H, 5.97; C, 76.12. Found: H, 5.63, 5.57; C, 76.16, 76.05. *Mol. wt.* Calcd. for $C_{17}H_{16}O_3$: mol. wt., 268. Found: mol. wt. (freezing point method), 273, 273.

The analysis proved this compound to be an hydroxybenzoate of phenylbutadiene. The hydroxybenzoate is very soluble in most organic solvents: benzene, chloroform, carbon tetrachloride, methyl and ethyl alcohol, ether, glacial acetic acid and acetone; but is only slightly soluble in hot low-boiling ligroin, and insoluble in water, dilute alkali and dilute acid. It may be recrystallized by adding ligroin to a benzene solution, water to a methyl alcohol solution, or by allowing the compound to crystallize slowly from hot low-boiling ligroin.

That the hydroxybenzoate was formed directly in the chloroform solution of perbenzoic acid and phenylbutadiene, and not from an esterification of the dihydroxy derivative which might have resulted from the hydrolysis of the oxide in alkaline solution, was established in two ways. (1) The pure monoxide was shaken with six times its equivalent of sodium benzoate in 5% sodium hydroxide solution for twenty-four hours, but no hydroxybenzoate could be detected. (2) The chloroform was evacuated from a portion of an original reaction mixture. The resulting pasty mass of solid, oil and a small amount of solvent was not treated with alkali but filtered to remove benzoic acid. As the filtration was very slow, more solvent was removed while filtering and crystals separated out in the filtrate. The first crystals obtained proved to be benzoic acid, but after several filtrations the crystals obtained, on recrystallization from hot low-boiling ligroin, melted at 79°, and a mixture with known hydroxybenzoate melted at 81.5°. This proved that the hydroxybenzoate was formed by the direct addition of perbenzoic acid to phenylbutadiene.

The hydroxybenzoate was subjected to ozonization in a manner entirely analogous to that described in previous work.[9] One gram of the hydroxybenzoate gave 0.08 g. of the semicarbazone of benzaldehyde and 0.63 g. of benzoic acid. This corresponds to an 82.5% yield of benzoic acid calculated on the basis of two moles of benzoic acid for each mole of hydroxybenzoate.

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[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 30.

[14] The chloroform solution of perbenzoic acid, prepared by the method of Tiffeneau, always contains benzoic acid.

The hydroxybenzoate did not absorb bromine readily at room temperature but on boiling with bromine in carbon tetrachloride solution a dibromide, m. p. 154–155°, was formed.

Anal. Calcd. for $C_{17}H_{16}O_3Br_2$: H, 3.74; C, 47.66; Br, 37.38. Found: H, 3.71, 3.79; C, 47.49, 47.69; Br, 37.38, 37.34.

The dibromide is soluble in benzene, ether, methyl and ethyl alcohol, chloroform and carbon tetrachloride, and only slightly soluble in hot low-boiling ligroin.

The Preparation of the Dimer of Phenylbutadiene Monoxide.—The hydroxybenzoate was heated on the steam-bath for twenty-four hours with 30% sulfuric acid. The reaction mixture was made alkaline and shaken with ether. A white crystalline product remained suspended in the ether layer. This was removed and carefully washed with ether. The pure crystals melted at 192°.

Anal. Calcd. for $(C_{10}H_{10}O)_2$: H, 6.90; C, 82.15. Found: H, 7.00, 7.33; C, 82.18, 82.35. *Mol. wt.* Calcd. for $(C_{10}H_{10}O)_2$: mol. wt., 292. Found: mol. wt. (boiling point method), 303, 307.

Benzoic acid was obtained when the alkaline extract was acidified.

The dimer of the monoxide is very slightly soluble in most of the common organic solvents but sufficiently soluble in warm ether to permit recrystallization from boiling ether.

The dimer of the monoxide of phenylbutadiene (0.45 g.), dissolved in chloroform, was ozonized for twelve hours. Most of the material (0.30 g.) was recovered unchanged, and 0.1 g. of benzoic acid, which represents 80% of the material decomposed by ozonization, was isolated.

The dimer of the monoxide of phenylbutadiene was brominated by boiling with bromine in chloroform solution. The product, a tetrabromide of the dimer, melts at 220°.

Anal. Calcd. for $C_{20}H_{20}O_2Br_4$: H, 3.27; C, 39.23. Found: H, 3.36, 3.34; C, 39.01, 39.17.

The Preparation of 3,4-Dihydroxyphenylbutadiene.—The hydroxybenzoate was shaken for three-quarters of an hour with twice the equivalent amount of 10% sodium hydroxide. The mixture was extracted with large volumes of ether, the ether extract dried over anhydrous sodium sulfate, the drying agent removed by filtration and the ether evaporated on the steam-bath. The oily mass that remained was taken up in hot benzene, from which solution crystals of the dihydroxy derivative, m. p. 74°, separated on cooling.

Anal. Calcd. for $C_{10}H_{12}O_2$: H, 7.37; C, 73.13. Found: H, 7.12, 7.38; C, 73.08, 73.11. *Mol. wt.* Calcd. for $C_{10}H_{12}O_2$: mol. wt., 164.1. Found: mol. wt. (boiling point method), 164.8, 167.5.

The dihydroxy derivative has also been obtained from the alkaline extract which results from the purification of the hydroxybenzoate.

The dihydroxy derivative is very soluble in hot benzene, soluble in methyl and ethyl alcohol, ether, acetone, warm acid and warm alkali, very slightly soluble in hot low-boiling ligroin and cold benzene, and insoluble in carbon tetrachloride, chloroform and cold water.

One gram of the dihydroxy derivative was ozonized for five hours. The ether extract of the alkaline solution yielded benzaldehyde, which was identified by the formation of its semicarbazone (0.2 g.). Benzoic acid (0.4 g.) was recovered from the alkaline extract. The amount of the two products isolated corresponds to 74.2% of the sample ozonized.

The dihydroxy derivative absorbed one mole of bromine in ligroin solution at room temperature to form a dibromide of the dihydroxy derivative, m. p. 94°.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: H, 3.73; C, 37.04. Found: H, 3.41, 3.68; C, 36.87, 36.97.

The dibromide of the dihydroxy derivative has the same melting point as the dibromide of phenylbutadiene but a mixture of the two melts at 86°. The dibromide of the dihydroxy derivative is much less soluble in ligroin than is the dibromide of phenylbutadiene.

The dihydroxy derivative was dissolved in ether and treated with five times the equivalent amount of phosphorus tribromide. The mixture was allowed to stand overnight, and the remaining phosphorus tribromide decomposed with ice. The water layer was extracted with ether and the ether was vaporized. The solid 3,4-dibromide of phenylbutadiene, m. p. 94°, remained. A mixture of this material with the known 3,4-dibromide of phenylbutadiene also melted at 94°. The dihydroxy derivative was treated in an analogous manner with phosphorus pentabromide. The product obtained was the tetrabromide of phenylbutadiene, m. p. 146°. A mixture with known tetrabromide of phenylbutadiene also melted at 146°.

The dihydroxy derivative was dehydrated to the dimer of the monoxide of phenylbutadiene, m. p. 192°, when an ether solution was treated with phosphorus pentoxide. The same product was isolated when the dihydroxy derivative was heated with 30% sulfuric acid at 100° for four hours in a bomb tube.

The Preparation of the Monoxide of Phenylbutadiene.—The hydroxybenzoate, in a methyl alcohol solution to which a few drops of dilute hydrochloric acid were added, was heated in a bomb tube at 120–130° for four to five hours. The methyl alcohol solution was then removed, a large volume of water was added and the mixture extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered and the major portion of the ether removed by means of suction. The remaining oil was distilled under reduced pressure. The fraction which distilled at 88° under 1 mm. pressure was a monoxide of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{10}O$: H, 6.90; C, 82.15. Found: H, 7.02, 7.29; C, 82.16, 82.36. *Mol. wt.* Calcd. for $C_{10}H_{10}O$: mol. wt., 146. Found: mol. wt. (freezing point method), 142.

One gram of the monoxide of phenylbutadiene was ozonized for five hours. Benzoic acid (0.45 g.) and the semicarbazone of benzaldehyde (0.13 g.) were isolated. The amount of the products isolated represented 65.4% of the material ozonized.

The monoxide of phenylbutadiene was warmed with 30% sulfuric acid on the steam-bath and the resulting viscous oil extracted with ether. From the ether extract the dimer of the monoxide of phenylbutadiene, m. p. 192°, was obtained.

The dry hydroxybenzoate was heated at atmospheric pressure for a short time. Most of the benzoate remained unchanged but a small amount of it was decomposed to the monoxide of phenylbutadiene and benzoic acid.

As has already been stated, small amounts of the monoxide oil always accompanied the hydroxybenzoate in the original reaction mixture.

Oxidation at 25°

Preparation of the Dioxidation Products.—*Cis*-phenylbutadiene was added to a slight excess of two equivalents of perbenzoic acid in chloroform solution at 25° and allowed to stand at that temperature until iodimetric titration indicated that no perbenzoic acid remained. This required eighteen to twenty hours. The resulting mixture was treated as described above for the hydroxybenzoate. The oil which remained after the ether was removed was distilled under reduced pressure. At 97° under 1 mm. pressure a small amount of dioxide oil was distilled.

Anal. Calcd. for $C_{10}H_{10}O_2$: H, 6.22; C, 74.04. Found: H, 6.06, 6.35; C, 74.23, 74.06.

The residue in the distilling flask was taken up in benzene and the solution allowed to stand overnight. Crystals of a dihydroxydibenzoate separated and were recrystallized from hot benzene; their melting point after recrystallization was 186°.

Anal. Calcd. for $C_{24}H_{22}O_6$: H, 5.42; C, 70.93. Found: H, 5.20, 5.35; C, 70.86, 70.75. *Mol. wt.* Calcd. for $C_{24}H_{22}O_6$: mol. wt., 406. Found: mol. wt. (boiling point method), 371.4.

The dibenzoate is only slightly soluble in most organic solvents but moderately soluble in chloroform and acetone.

Summary

1. The 3,4-hydroxybenzoate of phenylbutadiene was isolated as the primary product of the oxidation of *cis*-phenylbutadiene by means of perbenzoic acid, when the reaction was carried out at 0°. A dihydroxybenzoate was obtained from the same reagents at 25°.

2. The 3,4-hydroxybenzoate of phenylbutadiene was hydrolyzed with alkali to 3,4-dihydroxyphenylbutadiene and derivatives of the dihydroxy compound were prepared.

3. The 3,4-hydroxybenzoate of phenylbutadiene was decomposed by acids to the monoxide or the dimer of the monoxide of phenylbutadiene. The product obtained depended upon the acid used and the conditions under which the reaction took place.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ORIENTING INFLUENCES IN THE BENZENE RING. THE SULFONATION OF BENZOIC ACID[1]

BY JOHN S. REESE IV

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Generally speaking, previous work has shown that benzoic acid may be sulfonated readily with strong sulfuric acid at high temperatures (*ca.* 200°) and by long duration of heating (two to twenty-four hours).[2] In this way about 90% of the product is the *m*-sulfobenzoic acid and the balance is the para isomer. Furthermore, Maarse,[2] incidental to a lengthy investigation of this problem, demonstrated that the meta isomer may be converted under the ordinary reaction conditions into the para isomer

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[1] From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy. Presented before the Division of Organic Chemistry at the 82d Meeting of the American Chemical Society, Buffalo, N. Y., September, 1931.

[2] Maarse, *Rec. trav. chim.*, **33**, 207–238 (1914).