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THE OXIDATION OF TRIBROMORESORCINOL[1]

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A study of the oxidation of resorcinol and its derivatives is interesting because of the light which it may throw upon the mechanism of the oxidation of phenols in general, a subject already largely illuminated by the researches of Pummerer,[2] Goldschmidt,[3] Hunter[4] and others, and because of the possibility that *m*-quinones may be produced. No *m*-quinones are known. If products from the oxidation of resorcinol and its derivative are isolated and characterized and found to be not *m*-quinones, then the results will show us how the molecules have evaded the possibility of *m*-quinone formation and will, to that extent, increase our understanding of the factors which determine stable structures in aromatic and related compounds.

The oxidation of resorcinol does not appear to have been studied. Henrich, Schmidt and Rossteutscher[5] studied the oxidation by air of orcinol in alkaline solution and although they did not establish the structure of the primary oxidation product they showed that it yielded on reduction a substance which was probably pentahydroxyditolyl. Stenhouse[6] oxidized trichloro-orcinol with alkaline potassium ferricyanide and believed that he isolated a *p*-quinone, $C_7H_4Cl_2O_3$, which reduced to a hydroquinone, $C_7H_6Cl_2O_3$. He reported that he had secured corresponding results with tribromo-orcinol, trichlororesorcinol and tribromoresorcinol, but did not describe the experiments or the compounds. We find that alkali has a very destructive effect upon tribromoresorcinol,[7] and have had no success with ferricyanide as an oxidizing agent. Meyer and Desamari[8] attempted by a number of methods to prepare a *m*-quinone from tribromoresorcinol, but recovered the substance unchanged after shaking it in ether solution with silver oxide and anhydrous sodium sulfate, after boiling in benzene solution with lead dioxide, and after treating with nitric acid in cold glacial acetic acid solution. By the use of nitric acid in

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[1] A summary of the Doctor's Dissertation of Julian W. Hill, Massachusetts Institute of Technology, June, 1928.

[2] Pummerer and others, *Ber.*, **47**, 1472, 2957 (1914); **52**, 1392, 1403, 1414, 1416 (1919); **55**, 3116 (1922); **58**, 1808 (1925); **59**, 2161 (1926).

[3] Goldschmidt and others, *ibid.*, **55**, 3194, 3197 (1922); **56**, 1963 (1923).

[4] Hunter and others, THIS JOURNAL, **38**, 1761 (1916); **39**, 2640 (1917); **43**, 131, 135, 151 (1921); **48**, 1608, 1615 (1926).

[5] Henrich, Schmidt and Rossteutscher, *Ber.*, **48**, 483 (1915).

[6] Stenhouse, *ibid.*, **13**, 1305 (1880).

[7] *Cf.* Jackson, *Am. Chem. J.*, **18**, 117 (1896).

[8] Meyer and Desamari, *Ber.*, **42**, 2814 (1909).

warm glacial acetic acid solution, they converted tribromoresorcinol into 2-bromo-4,6-dinitroresorcinol.

We have isolated three products from the oxidation of tribromoresorcinol with aqueous chromic acid and have established their relationships and probable structure.

The methods described by Benedikt[9] for the preparation of tribromoresorcinol were found to give a poor yield (65% in the best experiment) and recrystallization from dilute alcohol gave pink crystals. We have found that crystallization from chloroform yields a white product and that bromination in that medium gives pure material in practically theoretical yield. The resulting tribromoresorcinol crystallized from chloroform in white needles, m. p. 111°, and was identified by analysis.

The first oxidation experiments were carried out by adding tribromoresorcinol with stirring to a fairly strong aqueous solution of chromic acid. A brick-red crystalline powder formed at once, the mixture soon warmed up with frothing and the reaction was stopped by diluting with a large volume of water. The solid matter, recrystallized from benzene, yielded some red crystals and some unchanged tribromoresorcinol, but mostly a varnish—and the amount of product was small. Much better results were secured by oxidation in a two-phase system. An approximately 10% solution of tribromoresorcinol in benzene was shaken from time to time during three hours with a slightly smaller volume of aqueous chromic acid solution (20% CrO_3) in a bottle cooled by immersion in freshly drawn tap water. Carbon dioxide was evolved and bromine set free. Crystals separated in both phases. Removed by filtration, washed with water and dried, the product consisted of a light red-brown crystalline powder equal to 30–37% of the weight of the tribromoresorcinol which was used. Under the polarizing microscope it was found to be a mixture of a large amount of red crystals with a red-yellow pleochroism and a relatively small amount of light-colored material.

Purification of the product presented many difficulties. It was soluble in benzene, ether and glacial acetic acid, and soluble and apparently stable in cold alcohol, though with hot alcohol it yielded acetaldehyde—and the solutions in ordinary, slightly moist solvents generally yielded varnishes. Perfectly dry benzene, distilled over sodium, was found to yield crystals. By fractional crystallization from this solvent, decantation and mechanical separation of the crystals, the crude material gave splendid red crystals with a blue reflection, about 60% of its weight, and light-colored material, about 8 or 9%. The latter material by crystallization from dry benzene yielded small, white, lustrous crystals and a very small amount of yellow crystalline matter.

The yellow substance melted at 211° and was identified as tribromo-

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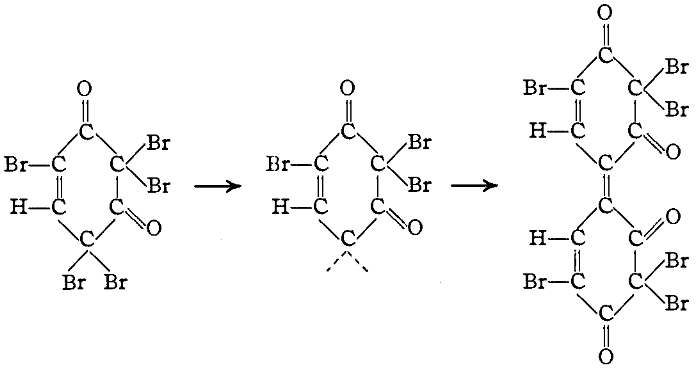
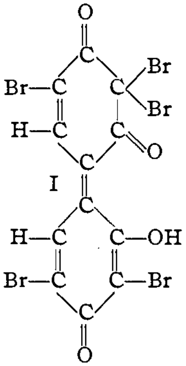
[9] Benedikt, *Monatsh.*, **4**, 227 (1883).

resoquinone by analysis and by comparison with known material prepared according to the method of Liebermann and Dittler[10] by heating pentabromoresorcinol at 157–160° in a current of dry carbon dioxide until bromine no longer came off, thus



The red-colored substance which is the principal product of the oxidation of tribromoresorcinol crystallized from benzene in crystals containing benzene of crystallization, a circumstance which materially hindered its characterization. It was obtained free from solvent by replacing the benzene with ether and then refluxing with low-boiling petroleum ether, and was found by analysis and molecular weight determination to have the composition, $C_{12}H_3O_4Br_5$. Its chemical properties and transformations indicate that it has one or another of the structures indicated below.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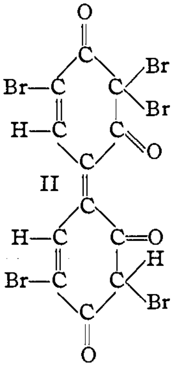
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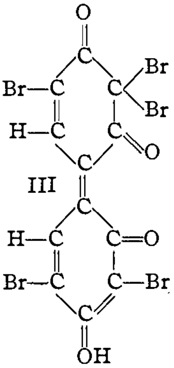
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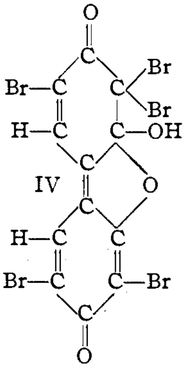
IV

The first three of these formulas may properly be regarded as representing one single tautomeric substance. Whether Formula IV, with the dibenzofuran[11] arrangement, really represents a substance different from this

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[10] Liebermann and Dittler, *Ann.*, **169**, 252 (1874).

[11] Behr, Arno and von Dorp, *Ber.*, **7**, 398 (1874), oxidized phenol to dibenzofuran, and Pummerer, *ibid.*, **58**, 1808 (1925), obtained a dibenzofuran derivative by the low-temperature oxidation of *p*-cresol by means of alkaline potassium ferricyanide.

one may perhaps be questioned. An attempt to prove the presence of an hydroxyl group by the formation of an acetyl derivative was unsuccessful—and we consider the structure represented by Formulas I, II and III as the more probable. We have named the substance rhodo-(brom)-resoquinone (literally, the red-colored quinone-like substance from the oxidation of brominated resorcinol).

Rhodo-(brom)-resoquinone crystallizes from benzene in deep red crystals which have at first a blue reflection but lose their luster rapidly and give off a portion of their benzene, retaining some of it very tenaciously. In a melting point tube the crystals swell up, give off their benzene at 105° and melt at about 220° with decomposition and blackening. Analysis for carbon, hydrogen and bromine indicated that different batches contained different amounts of benzene. The molecular compound of rhodo-(brom)-resoquinone with ether, $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$, crystallizes from ether in pyramidal crystals of a somewhat lighter shade of red than the benzene compound. The crystals retain their luster and do not lose ether on exposure to the air. After some months they turn brown and smell of acetaldehyde. On heating they bleach and finally melt with decomposition at about 215°. The molecular compound with carbon disulfide, $C_{12}H_3O_4Br_5{\cdot}{}^1/_4CS_2$, was identified by analysis. Compounds with bromoform and carbon tetrachloride were also prepared.

Rhodo-(brom)-resoquinone dissolves in dilute aqueous sodium hydroxide to form a dark green or black solution, and in concentrated sulfuric acid with a deep red color. It oxidizes the usual ketone reagents, hydrazine, semicarbazide, hydroxylamine, phenylhydrazine and dinitrophenylhydrazine, with the evolution of nitrogen. With reducing agents, sulfurous acid, sodium bisulfite, stannous chloride, metal and acid, hydrogen bromide and hydrogen iodide, it yields 3,5,3′,5′tetrabromo-2,4,2′,4′-tetrahydroxydiphenyl, identified by analysis of the substance and of its tetra-acetate for bromine and by mixed melting points of the two with known materials prepared by the reduction of tribromoresoquinone and subsequent acetylation.

In the first experiments rhodo-(brom)-resoquinone was reduced by passing sulfur dioxide into an alcohol suspension of the substance. It later appeared that the same result could be attained more rapidly and more conveniently by bubbling hydrogen bromide through a benzene solution or suspension. Bromine is liberated. Aqueous hydrobromic acid acts in the same way but much more slowly. An alcohol solution of hydrogen iodide acts rapidly, liberating iodine. A determination of the amount of iodine which was liberated supplied a means of ascertaining the oxidizing power of the substance and hence supplied further evidence of its structure.

Tribromoresoquinone was found to be reduced by the same treatment and an experiment was carried out with that substance as a check upon the accuracy of the method. The conversion of tribromoresoquinone into tetrabromotetrahydroxydiphenyl, that is, the change from $C_{12}H_2O_4Br_6$ to $C_{12}H_6O_4Br_4$, involves the addition of four hydrogen atoms and the removal of two bromine atoms, and hence requires six molecules of hydrogen iodide, thus

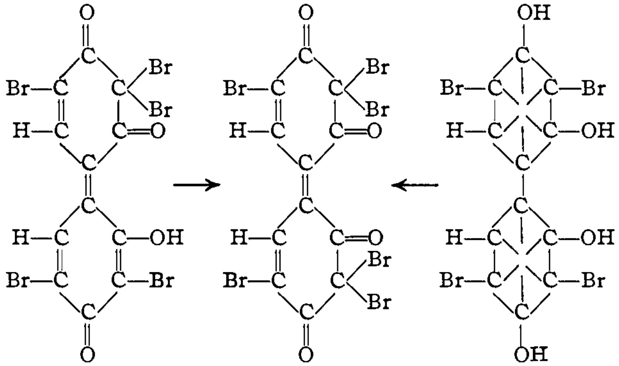
$$C_{12}H_2O_4Br_6 + 6HI \longrightarrow C_{12}H_6O_4Br_4 + 3I_2 + 2HBr$$

Similarly, if rhodo-(brom)-resoquinone has the formula which we suppose it to possess, its reduction by hydrogen iodide would take place as follows

$$C_{12}H_3O_4Br_5 + 4HI \longrightarrow C_{12}H_6O_4Br_4 + 2I_2 + HBr$$

Titrations with thiosulfate of the iodine liberated during the reduction of tribromoresoquinone and of solvent-free rhodo-(brom)-resoquinone (taken for convenience in weighing) gave results in agreement with the above equations. This establishes definitely the number of the hydrogen atoms in rhodo-(brom)-resoquinone, a number which is left in doubt by the elementary analysis. An experiment with rhodo-(brom)-resoquinone containing ether of crystallization gave a result which corresponds to the formula $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$ for the molecular compound.

Rhodo-(brom)-resoquinone yields the same reduction product as tribromoresoquinone, and the measurement of its oxidizing power suggests that it is intermediate between tribromoresoquinone and its reduction product. We find indeed that it is converted into tribromoresoquinone by the treatment by which Zincke and Schwabe[12] previously converted tetrabromotetrahydroxydiphenyl into tribromoresoquinone, namely, by the action of bromine in 50% aqueous acetic acid. The formulas show the close similarity between the compounds.



Rhodo-(brom)-resoquinone Tribromoresoquinone

Final proof that rhodo-(brom)-resoquinone is intermediate between tribromoresoquinone and its reduction product was found by producing it by the partial reduction of tribromoresoquinone. The reduction first

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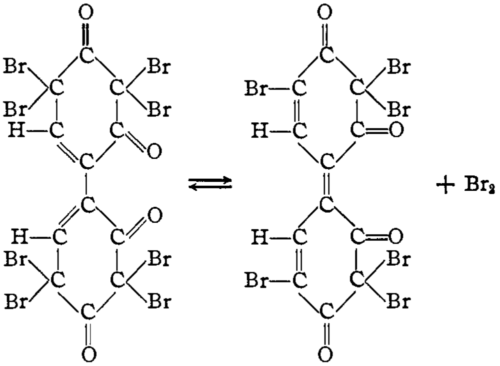
[12] Zincke and Schwabe, *Ber.*, **42**, 797 (1909).

came about by accident. Tribromoresoquinone was allowed to stand overnight with a solution of bromine in benzene, and crusts of red crystals of rhodo-(brom)-resoquinone were found the next morning on the sides and bottom of the vessel. On longer standing the red crystals disappeared and white crystals of tetrabromotetrahydroxydiphenyl were deposited. Rhodo-(brom)-resoquinone alone was found to yield the same reduction product under like conditions. The reduction of tribromoresoquinone first to rhodo(brom)-resoquinone and finally to tetrabromotetrahydroxydiphenyl was due in this case to hydrogen bromide produced by the action of the bromine on the benzene, for solutions containing these substances did not evolve hydrogen bromide as did a solution of bromine in benzene alone. Tribromoresoquinone is not altered by long contact with a solution of bromine in carbon tetrachloride in a dry vessel closed by a glass stopper. If a cork stopper is used, the cork is attacked by the bromine to produce hydrogen bromide, and the same changes occur as in benzene solution. With hydrogen iodide tribromoresoquinone is reduced at once to tetrabromotetrahydroxydiphenyl; it is not possible, as with hydrogen bromide, to stop at the intermediate stage of reduction which is represented by rhodo-(brom)-resoquinone.

When the molecular compounds of rhodo-(brom)-resoquinone are heated they slowly lose their color and at 160–190° are entirely bleached. The white compound which is thus produced was obtained in larger quantity by heating the benzene compound at 120° for several days—small, white needles from glacial acetic acid, m. p. 228–229°. Analysis gave results which correspond to the formula, $C_{12}H_3O_4Br_5$, indicating that the substance is isomeric or polymeric with rhodo-(brom)-resoquinone. The substance is sparingly soluble in the usual solvents and its molecular weight could not be determined. It dissolves slowly in glacial acetic acid with the production of a yellow color. It liberates much less iodine from alcoholic hydrogen iodide than does rhodo-(brom)-resoquinone and resists all attempts at bromination whether in glacial or dilute acetic acid, in chloroform or carbon tetrachloride, or with undiluted bromine. We have not been able to prove its structure.

The white product from the oxidation of tribromoresorcinol was obtained by the spontaneous evaporation of its benzene solution as small, white, lustrous crystals, m. p. 227–228° with decomposition. Analysis indicated the formula, $C_{12}H_2O_4Br_8$, and its properties and reactions warrant us in assigning it the structure of tetrabromoresoquinone. Boiled with glacial acetic acid it goes into solution; the liquid quickly turns yellow and then deep orange red, bromine is given off and the liquid on cooling deposits crystals of tribromoresoquinone. The heavily brominated tetrabromoresoquinone under these conditions drops off two bromine atoms to produce the more highly conjugated tribromoresoquinone, thus

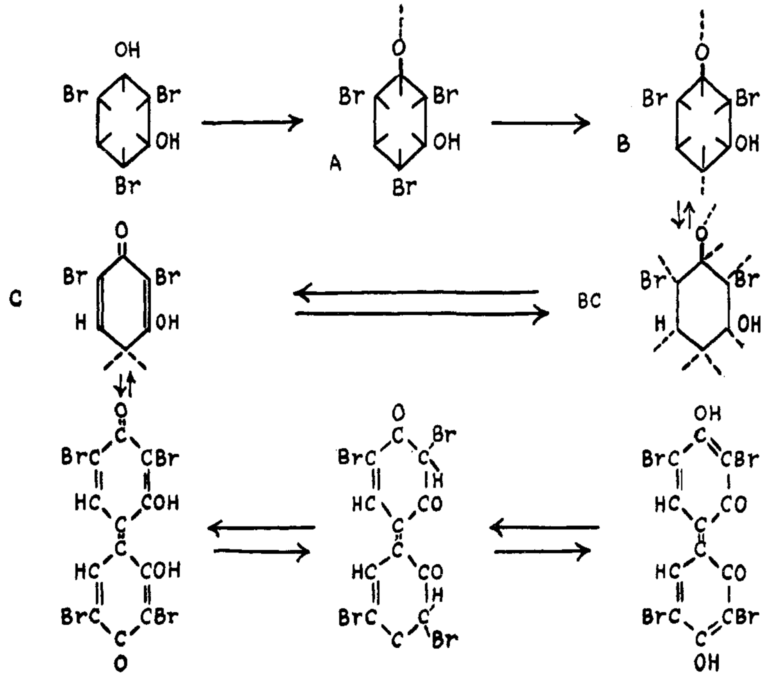


In benzene solution tetrabromoresoquinone shows but little tendency to give off bromine, yet the residues from the evaporation of such solutions to dryness are invariably tinged with yellow. When reduced in alcohol solution with aqueous stannous chloride, tetrabromoresoquinone yields 3,5,3′,5′-tetrabromo-2,4,2′,4′-tetrahydroxydiphenyl. Titration of the iodine liberated by the reaction of tetrabromoresoquinone on hydrogen iodide in alcohol solution showed that the reaction takes place as follows

$$C_{12}H_2O_4Br_8 + 8HI \longrightarrow C_{12}H_6O_4Br_4 + 4I_2 + 4HBr$$

The result served also to fix with certainty the hydrogen content of the substance, otherwise left in doubt because of the errors inherent in the determination of a small amount of hydrogen. Tetrabromoresoquinone is produced from tribromoresoquinone and from rhodo-(brom)-resoquinone when either of these substances is allowed to stand in contact with undiluted bromine. It is produced when tribromoresoquinone is shaken by machine for twenty-four hours with benzene and aqueous chromic acid containing bromine, under conditions similar to those which existed in the original oxidation experiment.

The Mechanism of the Reaction.—The work of Pummerer,[2] Goldschmidt[3] and Hunter[4] has shown it to be probable that the first step in the oxidation of phenols is the removal of hydrogen from the hydroxyl group, leading to the formation, at least momentarily, of a radical in which there is a free oxygen affinity, a radical of the sort which Hunter has designated Type A. Hunter's work has further made it probable that the formation of a radical of this type is followed, in the case of halogenated phenols, by the loss of halogen from the ring with the production of a (Type B) doubly unsaturated radical. Such Type B radicals may under oxidizing conditions yield *p*-quinones, which compounds Stenhouse, Hunter and others have indeed procured. In the absence of oxidizing agents they may combine with themselves, as Hunter found, to form polyphenylene oxides. They may also combine with themselves in another mode to form di-nuclear quinones, a possibility which is perhaps more evident if the radical represented by the Type B formula is formulated in another way (Type C below). Since Types B and C, if written with the partial valencies according to Thiele (BC below), have the same graphical representation, we think that any distinction between them is without a difference in fact and is entirely gratuitous. The action of chromic acid on tribromoresorcinol, in accordance with these hypotheses, would result in the liberation of free bromine and in the formation of a radical which would combine with itself to form the at present unknown dibromoresoquinone.



If dibromoresoquinone were a product of the oxidation of tribromoresorcinol, it would be expected to be brominated further under the conditions of our experiment. The substitution of one bromine atom would yield rhodo-(brom)-resoquinone, which would enter into molecular combination with the benzene which is present, would crystallize out and would to a large extent escape further action. If any of it should brominate, however, it would yield tribromoresoquinone and tetrabromoresoquinone, the substances which we have found. It seems probable that tribromoresoquinone was not present in the crude product of the oxidation and that the small quantity which we found was produced during the fractional crystallization by the spontaneous elimination of bromine from tetrabromoresoquinone.

Experiments

Experiments which are indicated with sufficient fullness in the foregoing are not again described in this section. Experiments are reported in the order in which their results are discussed in the first section of the paper.

Preparation of Tribromoresorcinol.—One hundred grams of resorcinol was suspended in 1500 cc. of chloroform and 432 g. of bromine was added slowly from a dropping funnel while the mixture was mechanically stirred. The clear red liquid was boiled under reflux for about an hour until it had become light yellow in color and hydrogen bromide was no longer evolved. It was treated with decolorizing carbon, distilled to one-third its volume and allowed to cool and crystallize. Concentration of the mother liquors yielded more material and the last crops were of a faint pink color. The product crystallized in handsome white needles, m. p. 111°, and was obtained in practically theoretical amount. Recrystallization from chloroform failed to raise the melting point but removed every trace of color.

Anal. Subs., 0.1964: CO_2, 0.1508; H_2O, 0.0171. Subs., 0.1230: AgBr, 0.2009. Calcd. for $C_6H_3O_2Br_3$; C, 20.69; H, 0.86; Br, 69.12. Found: C, 20.95; H, 0.97, Br, 69.51.

Isolation of the Oxidation Products.—The oxidation of tribromoresorcinol was carried out in batches, in the manner described earlier, 200 cc. of a 10% solution of the substance in benzene (previously treated with chromic acid and washed with water) and 125 cc. of aqueous chromic acid being used for each run. Gases were given off which contained carbon dioxide, as evidenced by turbidity with baryta water. After about forty-five minutes the two phases emulsified and crystalline material began to separate. Experiment showed that the yield of product did not increase after three hours, at the end of which time from 6 to 7.5 g. of crude material was obtained from each batch. The mother liquor contained free bromine, as shown by the production of tribromo-aniline, m. p. 120°, when it was distilled into aniline water.

The crude product contained a small amount of insoluble, dark-colored material which was discarded. One hundred and fifty grams, worked up as already described, yielded 90 g. of red crystals, 12 g. of light-colored material and 25 g. of residues which it was not practicable to work up. The working up of the light-colored material yielded a very small amount of the yellow constituent. The red and yellow substances were purified further by recrystallization from hot dry benzene. The white substance was obtained pure by dissolving it in a large volume of benzene and concentrating slowly. Its solubility varied very little with temperature but it separated in crystals as the volume diminished.

The Yellow Substance—Tribromoresoquinone.—*Anal.* Subs., 0.1194: AgBr, 0.1947. Calcd. for $C_{12}H_2O_4Br_6$: Br, 69.56. Found: Br, 69.40.

Rhodo-(brom)-resoquinone.—The red crystals which resulted from the fractional crystallization from benzene were shown to contain benzene by decomposing 4.5 g. of the material with aqueous potassium hydroxide and distilling into an ice-cooled receiver. The solid portion of the distillate melted at about 7°, occupied a volume of 0.90 cc. at room temperature, boiled at 79°, and on nitration yielded *m*-dinitrobenzene, m. p. 89.5°. Two samples prepared at different times gave analytical results which correspond fairly well to one and to one-half equivalent of benzene, respectively, but the agreement is perhaps fortuitous.

Anal. Subs., 0.1976: CO_2, 0.2437; H_2O, 0.0302. Subs., 0.1916, 0.1867: AgBr, 0.2642, 0.2570. Calcd. for $C_{12}H_3O_4Br_5 \cdot C_6H_6$: C, 31.35; H, 1.30; Br, 58.05. Found: C, 33.64; H, 1.71; Br, 58.68, 58.58.

Anal. Subs., 0.1726, 0.2001: CO_2, 0.1809, 0.2073; H_2O, 0.0196, 0.0221. Subs., 0.1315, 0.1452, 0.1597: AgBr, 0.1858, 0.2061, 0.2255. Calcd. for $C_{12}H_3O_4Br_5.{}^1/_2C_6H_6$: C, 27.69; H, 0.92; Br, 61.54. Found: C, 28.59, 28.26; H, 1.27, 1.24; Br, 60.13, 60.40, 60.09.

The molecular compound of rhodo-(brom)-resoquinone with ether was prepared by extracting a portion of the benzene compound in a Soxhlet extractor with ether which had been previously distilled over sodium. After a time crystals began to separate from the boiling liquid in the flask. When all of the material had been dissolved from the thimble, the crystals in the flask were removed. Another crop of excellent crystals was obtained by evaporating the mother liquor almost to dryness in a vacuum over sulfuric acid. Three and five-tenths grams of the substance, decomposed by cold aqueous potassium hydroxide, yielded about 0.3 cc. of a liquid which smelled like ether and boiled at 35–37°. The alkaline liquid on distillation gave no evidence of benzene.

Anal. Subs., 0.1878, 0.2226: CO_2, 0.1916, 0.2286; H_2O, 0.0323, 0.0390. Subs., 0.1195, 0.1243, 0.1444: AgBr, 0.1651, 0.1705, 0.1985. Calcd. for $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$: C, 28.03; H, 1.90; Br, 58.40. Found: C, 27.83, 28.01; H, 1.92, 1.96; Br, 58.79, 58.37, 58.50.

The molecular compound with carbon disulfide was prepared from the benzene compound in the same way by the use of a Soxhlet extractor.

Anal. Subs., 0.01617, 0.01670: CO_2, 0.01395, 0.01451; H_2O, 0.00101, 0.00131. Subs., 0.1480: AgBr, 0.2213; $BaSO_4$, 0.0279. Calcd. for $C_{12}H_3O_4Br_5{\cdot}{}^1/_4CS_2$: C, 23.3; H, 0.48, Br, 63.5; S, 2.54. Found: C, 23.5, 23.7; H, 0.69, 0.87; Br, 63.6; S, 2.59.

Rhodo-(brom)-resoquinone free from combined solvent was obtained by boiling the ether compound with dry, low boiling, petroleum ether. The temperature of the heating bath did not exceed 45°. At the end of an hour and three-quarters the crystals had entirely disintegrated to a red powder. This was removed and dried in a vacuum.

Anal. Subs., 0.1631, 0.1718: CO_2, 0.1405, 0.1470; H_2O, 0.0088, 0.0102. Subs., 0.1191, 0.1418: AgBr, 0.1830, 0.2265. Calcd. for $C_{12}H_3O_4Br_5$: C, 23.56; H, 0.49; Br, 65.47. Found: C, 23.50, 23.34; H, 0.60, 0.66; Br, 65.39, 65.22.

Mol. wt. Subs., 0.0756, 0.0736; benzene, 20.32, 20.29; ΔT, 0.032°, 0.031°. Calcd.: 611. Found: 616, 620.

Reduction of Rhodo-(brom)-resoquinone.—Ten grams of rhodo-(brom)-resoquinone with benzene of crystallization was dissolved in a mixture of 140 cc. of alcohol and 40 cc. of water, and sulfur dioxide was bubbled in until the liquid was light yellow. A precipitate separated and a further quantity of crystals appeared when the liquid was diluted with water. The yield of crude tetrabromotetrahydroxydiphenyl amounted to 5 g. of fine, violet-tinted crystals. Recrystallized from dilute alcohol with the use of decolorizing carbon, it yielded the pure product, silky white needles which melted at 277–278° after darkening at 240°.

Anal. Subs., 0.0980, 0.0960, 0.1087: AgBr, 0.1375, 0.1345, 0.1520. Calcd. for $C_{12}H_6O_4Br_4$: Br, 59.90. Found: Br, 59.71, 59.62, 59.51.

Three and one-half grams of tetrabromotetrahydroxydiphenyl was acetylated by boiling for a short time with 10 cc. of acetyl chloride and a few drops of concd. sulfuric acid and yielded 3.5 g. of the tetra-acetate, m. p. 194.5° after recrystallization from alcohol.

Anal. Subs., 0.1210, 0.1224: AgBr, 0.1294, 0.1311. Calcd. for $C_{20}H_{14}O_8Br_4$: Br, 45.58. Found: Br, 45.51, 45.57.

Iodimetric Titration of Tribromoresoquinone and Rhodo-(brom)-resoquinone.—The sample was dissolved as far as possible in 10 cc. of alcohol. Five cc. of 10% sulfuric acid and 1 cc. of 50% potassium iodide solution were then added with swirling. A white, crystalline precipitate of potassium sulfate separated. After standing for a short time, the mixture was diluted with 50 cc. of water. Most of the precipitate dissolved. The diluted solution was then titrated with standard sodium thiosulfate solution. Just before the disappearance of the yellow color, starch solution was added and the liquid was titrated to the disappearance of the blue tint. Experiment showed that if less alcohol was used, the sample blackened when potassium iodide was added. If much more alcohol was used, no blue color was produced on the addition of the starch solution.

Anal. Tribromoresoquinone. Subs., 0.1356, 0.1147: 29.75, 25.32 cc. of 0.0394 *N* $Na_2S_2O_3$. Calcd.: 1.179, 0.997 cc. of *N* $Na_2S_2O_3$. Found: 1.172, 0.998.

Anal. Rhodo-(brom)-resoquinone free from solvent. Subs., 0.0752, 0.1458: 11.25, 21.55 cc. of 0.0441 *N* $Na_2S_2O_3$. Calcd.: 0.493, 0.956 cc. of *N* $Na_2S_2O_3$. Found: 0.496, 0.950.

Anal. Rhodo-(brom)-resoquinone with ether. Subs., 0.1877, 0.1079: 24.90, 14.40 cc. of 0.0441 *N* $Na_2S_2O_3$. Calcd. for $C_{12}H_3O_4Br_5{\cdot}C_4H_{10}O$: 1.096, 0.630 cc. of *N* $Na_2S_2O_3$. Found: 1.098, 0.635.

Bromination of Rhodo-(brom)-resoquinone.—One gram of rhodo-(brom)-resoquinone with benzene of crystallization was suspended in 15 cc. of 50% aqueous acetic acid and 1 cc. of bromine in 2 cc. of glacial acetic acid was added. The solid matter very soon turned yellow. After an hour it was removed, washed with water, dried in a vacuum over phosphorus pentoxide and recrystallized from benzene. The amber-colored crystals darkened at 190° and melted with decomposition at 210°. A mixture with known tribromoresoquinone of similar properties behaved in the same manner on heating.

Anal. Subs., 0.1266, 0.1429: AgBr, 0.2071, 0.2326. Calcd. for $C_{12}H_2O_4Br_6$: Br, 69.56. Found: Br, 69.62, 69.27.

Effect of Heating on Rhodo-(brom)-resoquinone.—A sample of rhodo-(brom)-resoquinone with benzene of crystallization was heated for one day at 95° and then for two days at 120°. The resulting light gray material after several crystallizations from glacial acetic acid yielded white crystals which melted at 228–229°. Although the substance appears to have the same composition as solvent-free rhodo-(brom)-resoquinone, it has only about one-half as much oxidizing power, as shown by iodimetric titration.

Anal. Subs., 0.01059, 0.01566: CO_2, 0.00902, 0.01348; H_2O, 0.00057, 0.00096. Subs., 0.0963, 0.0954: AgBr, 0.1477, 0.1466. Calcd. for $C_{12}H_3O_4Br_5$: C, 23.56; H 0.49; Br, 65.47. Found: C, 23.2, 23.5; H, 0.59, 0.68; Br, 65.27, 65.33. *Iodine Titration.* Subs., 0.01075, 0.01568, 0.02449: 3.40, 5.35, 10.30 cc. of 0.0105 *N* $Na_2S_2O_3$. Calcd.: 0.0705, 0.1028, 0.1606 cc. of *N* $Na_2S_2O_3$. Found: 0.0357, 0.0562, 0.1082.

Tetrabromoresoquinone.—*Anal.* Subs., 0.01718, 0.01303: CO_2, 0.01065, 0.00807; H_2O, 0.00100, 0.00099. Subs., 0.0940, 0.1006: AgBr, 0.1660, 0.1770. Calcd. for $C_{12}H_2O_4Br_8$: C, 16.9; H, 0.24; Br, 75.30. Found: C, 16.9, 16.9; H, 0.65, 0.84; Br, 75.15, 74.87. *Iodine Titration.* Subs., 0.0255, 0.0380: 27.21, 40.51 cc. of 0.00869 *N* $Na_2S_2O_3$. Calcd.: 0.240, 0.358 cc. of *N* $Na_2S_2O_3$. Found: 0.236, 0.352.

Conversion of Tetrabromoresoquinone to Tribromoresoquinone.—A small amount of tetrabromoresoquinone was boiled with 10 cc. of glacial acetic acid. The solution, yellow at first, became deep orange on boiling. The vapors turned starch–iodide paper blue. On cooling the liquid deposited orange needles, m. p. 203°. A sample of known tribromoresoquinone, recrystallized from glacial acetic acid, melted at 205°, and a mixture with the material from tetrabromoresoquinone melted at 204.5°. The appearance of the two under the microscope was identical.

Anal. Subs., 0.1263: AgBr, 0.2058. Calcd. for $C_{12}H_2O_4Br_6$: 69.56. Found: 69.34.

Conversion of Rhodo-(brom)-resoquinone and of Tribromoresoquinone to Tetrabromoresoquinone.—A small amount of solvent-free rhodo-(brom)-resoquinone was treated with 3 cc. of bromine, allowed to stand for two days and evaporated to dryness in a vacuum over caustic potash. The resulting material was ground up with carbon tetrachloride, washed with that solvent to free it from any traces of bromine, dried, taken up in benzene and evaporated to dryness at room temperature. The crystalline residue consisted of a mixture of white material with red crystals of rhodo-(brom)-resoquinone with benzene of crystallization. The white material was compared under the polarizing microscope with known tetrabromoresoquinone and found to be identical with it. Tetrabromoresoquinone is uniaxial negative with an ω-index of about 1.776 and an ϵ-index of about 1.700.

A similar experiment with tribromoresoquinone yielded a residue which consisted of a mixture of tetrabromoresoquinone with unchanged tribromoresoquinone.

A mixture of 1 g. of tribromoresoquinone, 13 cc. of 20% aqueous chromic acid, 20 cc. of benzene and 1 cc. of bromine was shaken by machine for twenty-four hours. The phases were separated and filtered and the residues were combined and recrystallized from benzene. The product consisted of small, white, lustrous crystals, m. p. 215°. A mixture with tetrabromoresoquinone, m. p. 227–228°, melted at 219–220°. A small amount of the material boiled with glacial acetic acid yielded a deep yellow solution. Examination under the polarizing microscope showed it to be tetrabromoresoquinone.

Summary

Tribromoresorcinol has been successfully oxidized by shaking a benzene solution of the substance with aqueous chromic acid.

Three products have been isolated. One of them, tribromoresoquinone, is known, having been prepared heretofore by another method. The other two, rhodo-(bromo)-resoquinone and tetrabromoresoquinone, are new. All three are dinuclear and yield the same tetrabromotetrahydroxydiphenyl on reduction.

The relationships among the three substances have been elucidated. Their oxidizing powers have been measured by titration of the iodine liberated from hydriodic acid and the results have given a precise indication of their hydrogen content.

The action of chromic acid on tribromoresorcinol appears to be first the oxidation of one hydroxyl group and the removal of one bromine atom from the nucleus. The resulting intermediate substance apparently doubles up to form the at present unknown dibromoresoquinone or 2,2′-dihydroxy-3,5,3′,5′-tetrabromodiphenoquinone. The products which have been isolated are brominated derivatives of this substance—rhodo-(brom)-resoquinone being formed by the substitution of one hydrogen atom by bromine, tribromoresoquinone by the substitution of two and tetrabromoresoquinone by the further *addition* of two bromine atoms.

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