bromo ether and a small amount of the dialkyl ether of butanediol-1,4.

A mechanism for this reaction has been offered based on the intermediate formation of chelate rings.

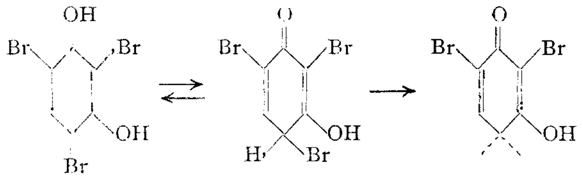
ITHACA, N. Y. RECEIVED JULY 17, 1933

[CONTRIBUTION NO. 97 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

The Pseudo-Quinoid Character of Tribromoresorcinol[1]

BY TENNEY L. DAVIS AND VALENTINE F. HARRINGTON

Tribromoresorcinol is definitely an oxidizing agent. Although it lacks the common quinoid character of being colored, it liberates iodine from hydriodic acid or from potassium iodide in alcohol solution in a manner which is characteristic of quinones. It oxidizes stannous chloride and sodium sulfite. It does not contain "positive bromine," for a solution of the substance in alkali does not brominate toluene sulfone amide. These facts, and others mentioned later, may be explained by supposing that tribromoresorcinol tautomerizes, as indicated below, to form a pseudo-quinone which breaks down into hydrogen bromide and a quinyl radical.



The first part of this hypothesis contains no novelty, for it is generally agreed that phenols exhibit this kind of tautomerism. The second part of the hypothesis is suggested by the fact that tribromoresorcinol, when warmed in aqueous solution or when heated above its melting point, gives off hydrogen bromide, and is confirmed by the circumstance that dark-colored amorphous polynuclear compounds are formed under these conditions, evidently by the combination of the quinyl radicals. We have not found any evidence which indicates that the breaking down is reversible and do not regard the quinyl as a "free" radical, but we have secured products which correspond both to the combination of the quinyl radicals with one another and to their reaction with a number of reagents.

The combination of two of the quinyl radicals would yield dibromoresoquinone or 3,3′,5,5′-tetrabromo-2,2′-dihydroxy-*p*-xenoquinone. An earlier paper[2] of this series has reported that the oxidation of tribromoresorcinol in benzene solution with aqueous chromic acid yields the products which would be expected from the action of bromine on dibromoresoquinone, a result which appears to be explained better by the present hypothesis than by that of the earlier paper.

Pyridine or alkali, in aqueous solution and in moderate amount, by removing hydrogen bromide from tribromoresorcinol, produces dark-colored amorphous polynuclear compounds; but dry pyridine in benzene, or aqueous alkali in large excess, by forming salts of the substance in its phenol form, reverse the equilibrium and suppress quinonization and the formation of the quinyl radical. The dark-colored substances correspond to the removal of two bromine atoms from each molecule of tribromoresorcinol. Whether the second bromine is removed by the hydrolysis of a bromine *ortho* to a quinone oxygen, or is lost by the spontaneous splitting out of hydrobromic acid following a second tautomeric change, we have not yet been able to determine.

Mild reduction of tribromoresorcinol with sodium sulfite or stannous chloride successively removes the bromine atoms *para* to the hydroxyl groups, and ceases with the production of 2-bromoresorcinol—a result which can be explained, without recourse to the quinyl radical, by supposing that the effect of the reducing agent is to add hydrogen to the conjugate system of the pseudo-quinone to form a compound which spontaneously loses hydrogen bromide, that this new compound in its turn quinonizes, etc. The intermediate reduction product, 2,6-dibromoresorcinol, has been isolated. Since tribromoresorcinol tends to lose hydrogen bromide any-

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(1) A summary of a portion of the Doctor's Dissertation of Valentine F. Harrington, Massachusetts Institute of Technology, June, 1931.

(2) Davis and Hill, THIS JOURNAL, **51**, 493 (1929); compare also Davis and Walker, *ibid.*, **52**, 358 (1930).

way, the possibility remains open that the reduction of the substance is really the reduction of the quinyl radical.

The oxidation of tribromoresorcinol monomethyl ether with chromic acid in glacial acetic acid solution yields 2-methoxy-3,5,6-tribromobenzoquinone without bromine being produced at the same time, a result which appears to be explained conveniently only by supposing that the quinyl radical takes part in the reaction. In the experiments of Davis and Hill, in which tribromoresorcinol was oxidized with aqueous chromic acid in the presence of benzene, bromine was actually produced and the products were those which would be expected where bromine was present. The absence of bromine in the present experiment indicates that the elements of hydrogen bromide are not oxidized off from the molecule of tribromoresorcinol monomethyl ether. We have to conclude that the hydrogen bromide splits off spontaneously, and hence that the corresponding quinyl radical has at least a momentary existence in the mixture. The quinyl radical is evidently oxidized to 2-methoxy-3,5-dibromobenzoquinone. It is not the bromination of this substance which yields the final product, for bromine is not present in the mixture. The substance, rather, combines with the hydrogen bromide which is present to form a hydroquinone derivative which is then oxidized by the chromic acid to yield the final methoxytribromobenzoquinone.

Experiments

Reaction with Iodides and Hydriodic Acid.—When tribromoresorcinol in 95% alcohol is boiled with sodium or potassium iodide, the liquid quickly becomes brown from the liberation of iodine. A series of quantitative experiments showed that acetic acid promotes the reaction, evidently by liberating hydriodic acid from the iodide, but that hydriodic acid hinders it if present in large excess. If no acetic acid is added, the reaction occurs with the hydriodic acid which is produced by the hydrolysis of the iodide, but the same hydrolysis produces alkali which reacts with the tribromoresorcinol to convert it into dark-colored polynuclear material, as will be described later. When only a little acid is present, the same effect occurs. In absolute alcohol solution but little hydriodic acid is produced by alcoholysis, and but little iodine is liberated.

An experiment in which the materials were refluxed together, while aliquot portions of the mixture were removed from time to time and titrated for iodine, showed that the reaction tends toward the removal of two bromine atoms from tribromoresorcinol, but that iodination commences before the reduction is complete.

Action of Pyridine on Tribromoresorcinol.—In benzene solution pyridine forms the salt of the phenol; in aqueous solution it splits off two molecules of hydrogen bromide and converts tribromoresorcinol into dark-colored amorphous polynuclear material.

Seventy grams of tribromoresorcinol was suspended in 500 cc. of water and 70 g. of pyridine in an equal volume of water was added. The mixture darkened immediately. After heating for two days on the steam-bath, analysis of an aliquot showed that the mixture contained 280 milliequivalents of bromide ion. The mixture yielded 42 g. of pyridine hydrobromide, 18 g. of tribromoresorcinol, and 23 g. of dark reddish brown amorphous material after washing the precipitate with 6 *N* hydrochloric acid and extracting with methyl alcohol. The dark-colored material was found to retain solvents with great tenacity, but was finally dried by heating in vacuum at 150°. It is insoluble in alcohol, ether, acetone, ethyl acetate, benzene and other hydrocarbons. It dissolves in alkali and is reprecipitated by acids apparently unchanged. It does not melt at a red heat, but burns readily in the air.

Anal. Calcd. for C_6HO_2Br: Br, 43.25. Found: Br, 39.90, 39.92.

The analysis indicates that slightly more than two equivalents of hydrogen bromide had been removed from each molecule of tribromoresorcinol, but is probably somewhat in error because of the difficulty of purifying the material. Oxidized with bromine in alkaline solution it yielded bromoform but no solid organic product. Efforts to reduce it with zinc and acetic acid, with aqueous hydriodic acid, and with anhydrous hydriodic acid in a sealed tube at 300° for twenty-four hours, were without apparent effect.

Effect of Alkali.—Tribromoresorcinol dissolves in aqueous sodium or potassium hydroxide to yield solutions which are colorless or pale yellow at first. If the ratio of alkali to phenol be greater than five, the solutions are stable indefinitely and the phenol may be recovered by acidification. If the ratio be two or less, the solutions darken in a few minutes and brown precipitates appear. With ratios between two and five, dark colored solutions result more or less rapidly, and acidification precipitates a mixture of unchanged tribromoresorcinol and brown material. Ten normal alkali gives a white precipitate of the disodium or dipotassium salt of tribromoresorcinol. The dipotassium salt was obtained in the form of square crystals by dissolving the crude salt in absolute alcohol and evaporating at −30° in a desiccator. The crystals decomposed in the desiccator within an hour at room temperature. They were stable for a day at 0°. On refluxing with an alcoholic solution of dimethyl sulfate they yielded tribromoresorcinol dimethyl ether in practically the theoretical amount.

The Brown Material by the Action of Alkali.—Thirty-four and seven-tenths grams (0.1 mole) of tribromoresorcinol heated on the steam-bath for twenty-four hours with 125 cc. of 2 *N* sodium hydroxide yielded a mixture which contained about 0.160 equivalent of bromide ion. The solution was filtered and the brown residue, extracted with water, benzene and chloroform and dried weighed 18 g. The brown material is infusible at a red heat but burns readily in the air. It is insoluble in chloroform, carbon tetrachloride and hydrocarbon solvents, but dissolves readily in alcohol, acetone, acetic acid and nitrobenzene.

In respect to its solubility in the last-named solvents it differs from the material which we have secured by the action of pyridine and agrees with that which Jackson[3] prepared by heating tribromoresorcinol with water. Its solution in acetic acid is decolorized by the action of zinc dust, but the color quickly reappears on contact with the air. Analysis indicates the removal of slightly less than two equivalents of hydrogen bromide from each molecule of tribromoresorcinol, but the results are possibly in error because of a small amount of adsorbed chloroform in the sample.

Anal. Calcd. for C_6HO_2Br: C, 38.9; H, 0.54; Br, 43.3. Found: C, 33.93, 34.09; H, 1.96, 1.86; Br, 45.0, 45.2.

Action of Sulfite.—Tribromoresorcinol shaken with an aqueous solution of an equimolecular quantity of sodium bisulfite, or of sodium sulfite whether or not in the presence of an excess of alkali, yields 2,4-dibromoresorcinol. With two molecules or more of the reducing agent it yields 2-bromoresorcinol. Sulfurous acid is practically without effect, even in a sealed tube at 100° for fifteen hours. 4,6-Dibromoresorcinol on treatment with sulfite is reduced to resorcinol, but the reaction is slower than that by which the bromine atoms in the 4 and 6 positions are removed from 2,4,6-tribromoresorcinol.

One-tenth of a mole (34.7 g.) of tribromoresorcinol, 0.1 mole (13 g.) of sodium sulfite, and 100 cc. of 2 *N* potassium hydroxide solution were shaken together. The tribromoresorcinol dissolved and a white voluminous precipitate appeared immediately. The mixture, acidified, boiled to remove sulfur dioxide, cooled and filtered, gave 10 g. of crystals melting at 86–89°. These, recrystallized from benzene, yielded pure 2,4-dibromoresorcinol, m. p. 92.8–93.7°.

Anal. Calcd. for $C_6H_4O_2Br_2$: Br, 59.67. Found: Br, 59.46, 59.42.

A similar experiment with water instead of potassium hydroxide solution gave a similar result.

Thirty-five grams of tribromoresorcinol was shaken with an excess of sodium sulfite solution and the liquid was acidified, warmed to expel sulfur dioxide and extracted with benzene. The extract yielded 7 g. of crystals which on recrystallization from benzene gave pure 2-bromoresorcinol, m. p. 101.2–102.0°.

Anal. Calcd. for $C_6H_5O_2Br$: C, 38.10; H, 2.67; Br, 42.30. Found: C, 38.25, 38.45; H, 2.7, 2.8; Br, 42.30, 42.22.

The substance is identified as 2-bromoresorcinol by the fact that it differs from 4-bromoresorcinol, m. p. 91–92°, prepared from 5-bromo-2,4-dihydroxybenzoic acid according to the method of Zehenter.[4] Van Hemmelmayr[5] has reported that the loss of carbon dioxide in boiling solution from 5-bromo-2,4-dihydroxybenzoic acid occurs at the rate of 19.67% per hour. We have boiled 47 g. of the acid with 2 liters of water for twenty-four hours, saturated the solution with salt, and extracted with ether, and secured only a 20% yield of 4-bromoresorcinol. The upper limit of our melting point is a degree higher than that reported by Zehenter.

Fifteen grams (0.0435 mole) of tribromoresorcinol was dissolved in 35 cc. of alcohol and the liquid was poured into 100 cc. of 3 *N* sodium sulfite solution. No precipitate appeared and the solution smelled strongly of sulfur dioxide. Reduction had taken place immediately, for analysis of aliquot portions showed that the solution contained 0.0860 equivalent of bromide ion and 0.135 equivalent of sulfite ion, which corresponds, within the error of the analysis, to the removal of two bromine atoms from each molecule of tribromoresorcinol and the oxidation of four equivalents (two moles) of sulfite.

One and seventy-five hundredths grams of 4,6-dibromoresorcinol (0.00653 mole), prepared by the bromination of resorcinol according to Zehenter,[4] was dissolved in 10 cc. of alcohol and added to 10 cc. of 3.47 *N* sulfite solution. The liquid was allowed to stand at room temperature and aliquot portions were analyzed. After one hour 0.0093 equivalent of bromine ion was found, after three hours 0.0115, and after twelve hours 0.0130. The solution, made alkaline and treated with benzoyl chloride in the usual way, yielded dibenzoylresorcinol, crystals from alcohol, m. p. 117°, identified by mixed melting point with a known sample.

Reduction with Stannous Chloride.—In strongly acid or strongly alkaline solutions stannous chloride is without action on tribromoresorcinol, but in solutions of such hydrogen-ion concentration that stannous hydroxide is present the bromine atoms in the 4 and 6 positions are removed completely and rapidly. The bromine atom in the 2 position is not affected.

Oxidation of Tribromoresorcinol Monomethyl Ether.—Thirty-six grams (0.1 mole) of tribromoresorcinol monomethyl ether was dissolved in 150 cc. of warm glacial acetic acid, and 75 cc. of a 6.5 *N* solution of chromic acid in glacial acetic acid was added from a dropping funnel while the mixture was stirred rapidly and its temperature maintained at about 50°. The mixture was warmed for half an hour at 60°. Analysis of an aliquot showed that it contained no free bromine and 0.050 equivalent of bromide ion. On drowning in a liter of cold water it yielded 23 g. of yellow material which, on recrystallization from acetic acid, gave 18 g. of pure 2-methoxy-3,5,6-tribromobenzoquinone, red crystals, m. p. 168–168.5°, identified by analysis and by mixed melting point with a sample prepared by the bromination of 2-methoxyhydroquinone.

Anal. Calcd. for $C_7H_3O_3Br_3$: Br, 63.98. Found: Br, 63.54, 63.44.

Preparation of 2-Methoxy-3,5,6-Tribromobenzoquinone.—Two and eight-tenths grams of 2-methoxyhydroquinone, prepared by the action of hydrogen peroxide on vanillin in alkaline solution according to the method of Dakin,[6] was dissolved in 50 cc. of chloroform and 5 cc. of bromine was added. The mixture, evaporated to dryness and recrystallized from glacial acetic acid, yielded 7 g. (90%) of pure 2-methoxy-3,5,6-tribromobenzoquinone. The substance dissolves very slowly in concd. sulfuric acid to form magenta colored solutions which retain their color on standing. With caustic alkali it gives salts of methylbromanilate, and with sulfurous acid is easily reduced to the corresponding hydroquinone.

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(3) Jackson, *Am. Chem. J.*, **18**, 117 (1896).

(4) Zehenter, *Monatsh.*, **8**, 296 (1887).

(5) Van Hemmelmayr, *ibid.*, **33**, 976 (1912); **34**, 374 (1913).

(6) Dakin, *Am. Chem. J.*, **42**, 77 (1909).

Methylbromanilate.—Three grams of 2-methoxy-3,5,6-tribromobenzoquinone, dissolved in 25 cc. of 2 *N* potassium hydroxide solution, warmed on the steam-bath, saturated with salt, cooled, and filtered, yielded 3 g. of fine long needles of potassium methylbromanilate, chocolate colored in the mass but colorless under the microscope. The same salt was prepared from 2-methoxy-3,5,6-tribromohydroquinone by dissolving 1 g. of that material in 10 cc. of 2 *N* potassium hydroxide solution and allowing to stand in the air for a day. The salt does not fuse at 350°. Its solutions in organic solvents are red, in water permanganate colored. Methylbromanilate was prepared from the potassium salt by dissolving 3 g. of the latter in 10 cc. of hot water, acidifying with 40 cc. of concd. hydrochloric acid, cooling, etc., and drying the red powder at 100° and finally in vacuum over potassium hydroxide. It does not melt at 350°.

Anal. Calcd. for $C_7H_4O_4Br_2$: Br, 51.25. Found: Br, 51.03, 51.00.

2-Methoxy-3,5,6-tribromohydroquinone.—Three and seventy-five hundredths grams of 2-methoxy-3,5,6-tribromobenzoquinone, reduced with sulfur dioxide in aqueous solution, yielded 3.5 g. (90%) of pure 2-methoxy-3,5,6-tribromohydroquinone, m. p. 175–176°, flat plates from benzene, diamond-shaped, probably monoclinic, having an extinction parallel to one of the edges, and having indices which "straddle" 1.72.

Anal. Calcd. for $C_7H_5O_3Br_3$: Br, 63.60. Found: Br, 63.55, 63.40.

Summary

Tribromoresorcinol evidently exists in the tautomeric pseudoquinoid form, for the effect of reagents upon it is the effect which the reagents would be expected to have upon the pseudoquinone or upon the 2,6-dibromo-3-hydroxybenzoquinyl-4, which corresponds to the loss of hydrogen bromide from that tautomer.

Tribromoresorcinol monomethyl ether on oxidation with chromic acid in glacial acetic acid solution yields methoxy-tribromobenzoquinone.

CAMBRIDGE, MASS.

RECEIVED JULY 20, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Reaction of Potassium Amide in Liquid Ammonia with Chloroethenes[1]

BY GEORGE H. COLEMAN AND ROY D. MAXWELL

Tolane together with diphenylvinyl ethyl ether was obtained by Buttenberg[2] by heating 1,1-diphenyl-2-chloroethene with sodium ethylate in a sealed tube at 180–200° for eight hours. It has been observed in this Laboratory that tolane is formed in good yields and in a short time when the same chloroethene is treated with potassium amide in liquid ammonia. The present work was undertaken in order to study this reaction more fully and to determine the effect of substituents in the phenyl groups.

The chloroethenes used were: (a) 1,1-diphenyl-2-chloroethene, (b) 1,1-di-*p*-tolyl-2-chloroethene, (c) 1,1-di-*p*-ethylphenyl-2-chloroethene, (d) 1,1-di-*p*-*n*-propylphenyl-2-chloroethene, (e) 1,1-di-*p*-*n*-butylphenyl-2-chloroethene, (f) 1,1-di-3,4-dimethylphenyl-2-chloroethene, (g) 1,1-di-*p*-methoxyphenyl-2-chloroethene. With compounds (b), (f) and (g), the substituents in the phenyl groups evidently have little effect on the reaction since the yields of the substituted tolanes were about the same as the yield of tolane. In each reaction the yield of crude product was 90 to 95% of the theoretical. The melting points of the crude products were only a few degrees below the melting points of the pure compounds. With the ethylphenyl, propylphenyl and butylphenyl compounds the crude yields were above 90% of the theoretical and did not contain halogen. The products were, however, oily in character and not more than 55% of pure recrystallized material could be isolated.

Undried liquid ammonia obtained directly from a tank was found to be as satisfactory for the reaction as that purified by distillation after treatment with metallic sodium. In contrast to the reaction with sodium ethylate, which required eight to ten hours, the reaction with potassium amide is complete in ten minutes or less. In one reaction sodium amide was used in place of potassium amide and was found to be just as effective.

The preparation of tolanes by this method directly from dichloroethanes was also tried. For this purpose 1,1-diphenyl-2,2-dichloroethane and 1,1-dibiphenyl-2,2-dichloroethane were used.

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[1] This communication is an abstract of a dissertation submitted by Roy D. Maxwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry at the State University of Iowa. A part of this work was presented at the Washington meeting of the American Chemical Society, March 1933.

[2] Buttenberg, *Ann.*, **279**, 327 (1894).