

Summary.

A convenient laboratory method is described for preparing rhamnose from "flavin," a commercial product rich in quercitrin. The flavin is hydrolyzed by boiling for 30 minutes with 10 parts of water and 0.5% sulfuric acid. The residue is washed free from sugar and the combined filtrates are neutralized with barium carbonate, decolorized, and concentrated under diminished pressure to a density of about 40% solids. The inorganic impurities are now precipitated by the addition of ethyl alcohol, and crystallization is readily accomplished by concentrating the filtrate to a density of 70–80% solids. The yield of rhamnose is 20–25% of the weight of flavin taken.

WASHINGTON, D. C.

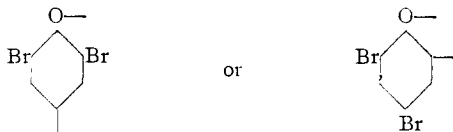
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. III. THE ACTION OF MERCURY ON TRIBROMOPHENOL BROMIDE.¹

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The purpose of the present paper is to show that the same result is attained by removing 2 atoms of bromine from tribromophenol bromide (tetrabromo-cyclo-hexadienone), as by removing a silver atom and a bromine atom from either of the silver salts of tribromophenol, *viz.*, the formation of residues²



which then polymerize to a compound of high molecular weight, $(C_6H_2Br_2O)_n$, for which the name poly-dibromo-phenylene oxide has been suggested.³

A secondary purpose is to show that the so-called "hexabromo-diphenoquinone" of Benedikt⁴ is not obtained by the action of tribromophenol bromide on the red silver salt of tribromophenol, as claimed by Kastle and Loevenhart.⁵

¹ The work described in this paper formed part of a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Guy Haines Woollett in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Cf. Hunter and Joyce, *THIS JOURNAL*, **39**, 2640 (1917).

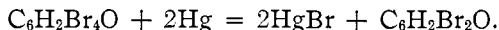
³ Hunter, *et al.*, *ibid.*, **38**, 1761 (1916).

⁴ Benedikt, *Ann.*, **199**, 128 (1879).

⁵ Kastle and Loevenhart, *Am. Chem. J.*, **27**, 21–52 (1902).

Poly-dibromo-phenylene Oxide from Tetrabromo-cyclo-hexadienone.

This is easily obtained in fair yield, by shaking mercury with a solution of tribromophenol bromide in benzene



Three g. of pure tribromophenol bromide in a test-tube, was dissolved in 25 cc. of benzene, about 2 cc. of mercury was added, and the tube was sealed, leaving very little air above the mixture. The mixture was shaken vigorously on a machine for $\frac{3}{4}$ of an hour, removed, and filtered. On addition of alcohol to the slightly yellow solution about 0.5 g. of amorphous substance was obtained, which was purified by solution and reprecipitation, dried, and analyzed for bromine.

Subs., 0.1061, 0.1097; AgBr, 0.1589, 0.1639.

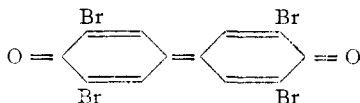
Calc for $(\text{C}_6\text{H}_2\text{Br}_2\text{O})_n$: Br, 64.00. Found: 63.73, 63.58.

An experiment with 5 g. of tribromophenol bromide in 125 cc. of benzene shaken one hour gave 1 g. of amorphous oxide.

One g. in 15 cc. of benzene shaken occasionally for 3 days gave 0.3 g. of oxide.

Since the only other amorphous product which could be expected was the "hexabromo-diphenoquinone" of Benedikt, which contains 72.7% of bromine, this was made according to his directions,¹ by heating tribromophenol bromide to between 130° and 140° in a current of dry carbon dioxide. It was found to resemble the poly-dibromo-diphenylene oxide in most of its properties, but its solubility in ether, noted by all who have worked with it, was so great as to distinguish it readily from the dibromoxide. The substance obtained by the action of mercury on tribromophenol bromide is then identical with the poly-dibromo-phenylene oxide obtained by the catalytic decomposition of phenol salts.

It was also obtained by Kastle and Loevenhart, by the action of sunlight on a carbon disulfide solution of the tetrabromo-cyclo-hexadienone, as shown by their analysis and their description of its properties, but they ascribed to it the tentative formula

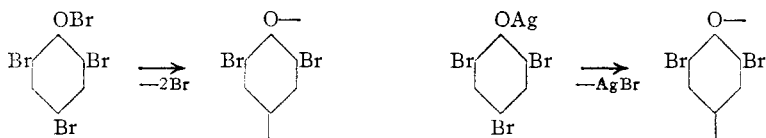


which belongs to the true tetrabromo-diphenoquinone, a red crystalline substance described long before by Magatti. We have repeated their experiments and compared the product with samples made from the silver salt. The 2 products agree in every respect.

Hence sunlight removes 2 atoms of bromine from tetrabromo-cyclo-hexadienone with the same result as treatment with mercury.

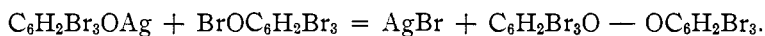
If the benzenoid formula is used for the tribromophenol bromide, the analogy between the methods of formation is clearer than with the quinoid.

¹ *Loc. cit.*



The Action of Tribromophenol Bromide on Silver Tribromophenolate.

According to Kastle-Loevenhart, the reaction between the silver salt and a chloroform solution of the phenol bromide is expressed by the equation



Both Benedikt's "hexabromo-phenoquinone" and the poly-dibromophenylene oxide are precipitated from chloroform solution by alcohol, and this is the circumstance which led to their error, for on addition of alcohol to their chloroform filtrate, they obtained a white amorphous precipitate, which without analysis they diagnosed as Benedikt's compound. The fact that all the silver appears as silver bromide was undoubtedly a contributing factor. The following series of experiments show conclusively, first, that the silver salt is catalytically decomposed into silver bromide and the expected dibromo oxide; second, that the tribromophenol bromide is left largely unchanged, a small amount changing to tar, and another small part probably becoming Benedikt's "hexabromo-diphenoquinone."

I. An Amorphous Compound is not Formed to the Amount Required by Kastle and Loevenhart's Theory.—Four and eight tenths g. of tribromophenol bromide was dissolved in about 20 cc. of chloroform to which 4.3 g. of the red-silver salt of tribromophenol was added rapidly and with good shaking. A transient greenish-blue color appeared as the red of the silver salt disappeared just as in the ordinary catalytic decompositions of the silver salt. It was allowed to stand for some time after the action appeared complete.

The precipitated silver halide was then filtered off and alcohol added to the filtrate. A white amorphous precipitate fell, just as was observed by Kastle and Loevenhart. It was collected, dried and found to weigh 2.3 g. If it were "hexabromo-phenoquinone," it should have weighed 6.7 g.; if it were the dibromo oxide, from the silver salt only, it should have weighed 2.7 g. At least a part of the missing 0.4 g. was in the alcohol chloroform mixture. For analyses, see next experiment.

II. The Tribromophenol Bromide Remains Unchanged Till Converted into Tribromophenol by Alcohol.—Four and four-tenths g. of the red silver salt and 4.1 g. of fresh phenol bromide were used in 75 cc. of chloroform. This reaction was run in the dark. After the reaction, the silver bromide was filtered off, alcohol was added to the filtrate, and the white amorphous compound was removed. The alcohol-chloroform solution, containing any unchanged phenol bromide, was then boiled to reduce the phenol bromide. A small amount of sticky orange colored tar precipitated. When all the chloroform was gone, water was added to the alcohol. A voluminous white precipitate appeared, which was crystallized from alcohol and water. It then melted at 91.5°, while tribromophenol melts at 93°. Part of it, dissolved in 0.2 *N* potassium hydroxide solution gave the red precipitate characteristic of tribromophenol, when it was treated with aqueous silver nitrate.

The white amorphous compound from this experiment was dried and analyzed for bromine by the Carius method.

Subs., 0.1071, 0.1028; AgBr, 0.1593, 0.1546.

Calc. for $(C_6H_2Br_2O)_n$: Br, 64.00. Calc. for $(C_6H_2Br_3O)_n$: Br, 72.70. Found: 63.30, 64.00.

These experiments seemed to prove that there was no action between the silver salt and the tribromophenol bromide, but that the silver salt was catalytically decomposed by the small amount of bromine resulting from the decomposition of the tribromophenol bromide. It is well known that this substance decomposes on standing in chloroform solution, with loss of bromine, and it has been shown in the first paper of this series that traces of any halogen are sufficient to start the decomposition of the silver salt. As a final test of this hypothesis, a reaction was carried out in chloroform solution, and all the solid products were determined.

III.—Two and five hundredths g. of tribromophenol bromide was dissolved in 100 cc. of dry alcohol-free chloroform, and 2.19 g. of the red silver salt of tribromophenol was suspended in it. It was allowed to stand till the reaction was complete.

The precipitated silver bromide was filtered, washed with chloroform, dried and weighed.

The chloroform solution, which according to Kastle and Loevenhart should have contained only Benedikt's "hexabromo-diphenoquinone," was boiled to $\frac{1}{2}$ its volume, and then treated with alcohol till no further precipitate resulted. This precipitate was collected, dried and weighed (A).

The filtrate from this, according to our views, contained tribromophenol bromide, which could not be present if Kastle and Loevenhart were correct. This filtrate was boiled to reduce any tribromophenol bromide to tribromophenol, and then evaporated partly. A small precipitate settled out, showing that some of A had remained in solution in the large volume of alcohol and chloroform, as is usual with poly-dibromophenylene oxide. This may be known as B. It was collected and dried.

The filtrate was treated with water, when the voluminous precipitate identified as tribromophenol in Expt. 2 resulted. This was also collected and weighed (C).

On evaporation of the last filtrate to dryness, a small amount of tar, D, was found. It was also weighed.

The results are tabulated below, together with the weights to be expected if our views are correct.

	Found. G.	Calc. G.
AgBr.....	0.955	0.94
A $(C_6H_2Br_2O)_n$	1.106	..
B $(C_6H_2Br_2O)_n$	0.146	..
Total A + B.....	1.252	1.25
C, $C_6H_2Br_3OH$	1.25	1.66
D, tar.....	0.15	..
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	3.607	3.85

Summary.

1. Poly-dibromo-phenylene oxide can be obtained by the action of mercury on tetrabromo-cyclo-hexadienone.

2. The mercury removes 2 bromine atoms, presumably forming

the same unsaturated residue— $C_6H_2Br_2O$ —which results from the catalytic decomposition of the silver salts of tribromophenol.

3. The compound obtained by Kastle and Loevenhart by the action of sunlight on tetrabromo-cyclo-hexadienone in carbon disulfide, is certainly poly-dibromo-phenylene oxide, again resulting from the loss of 2 atoms of bromine per molecule.

4. The action of tribromophenol bromide on silver tribromophenolate in chloroform does not give Benedikt's "hexabromo-diphenoquinone" as stated by Kastle and Loevenhart. Instead, the silver salt is catalytically decomposed by bromine resulting from the slow spontaneous decomposition of the tetrabromo-cyclo-hexadienone, which is otherwise unaffected.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. IV. THE CONSTITUTION OF THE AMORPHOUS OXIDES.¹

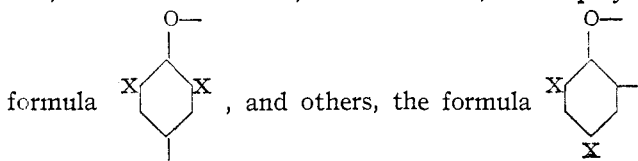
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In previous communications from this laboratory it has been shown that silver salts of symmetrically tri-halogenated phenols can be decomposed smoothly into silver halide and colorless amorphous compounds of high molecular weight, by the catalytic action of undiluted ethyl iodide,² or of small amounts of iodine.³

It has also been shown² that the amorphous bodies formed have exactly the same composition of the silver salt, minus silver halide; in other words, they are polymerization products of the residue $C_6H_2X_2O$, which results when silver halide is eliminated. On this account, it has been suggested, that they be called poly-dihalogen-phenylene oxides.

Furthermore, it has been shown⁴ that the halogen may be removed either from the *para*- or the *ortho*-position, so that from any sample of salt, residues are formed, some of which, before polymerization, have the



¹ The work described in this paper formed part of a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Guy Haines Woollett in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 38, 1761 (1916).

³ *Ibid.*, 38, 2474 (1916).

⁴ *Ibid.*, 39, 2640 (1917).