turning yellow on further heating, and at 232° decomposes with partial sublimation, leaving a small amount of a black residue.

Calc. for $C_6H_9O_2N_3$: N, 22.00%. Found: N, 21.87.

AUSTIN, TEXAS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

2,4-DIHYDROXYBENZOYLTETRACHLORO-*o*-BENZOIC ACID AND 2,3,4-TRICHLORO-6-HYDROXYXANTHONE-1-CARBOXYLIC ACID AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND W. A. ADAMSON.

Received May 23, 1918.

Historical.

Dihydroxybenzoylbenzoic acid was first prepared by Baeyer[1] in connection with his investigation of fluorescein. It was made by evaporating fluorescein in sodium hydroxide solution, containing 3 times its weight of sodium hydroxide, until the color becomes brownish yellow, dissolving in water and precipitating with acid. The substance was purified by dissolving in dilute sodium hydroxide solution, neutralizing with hydrochloric acid, heating to boiling, adding alcohol until the fluid became clear and allowing to crystallize. This product was found to have a melting point of about 200°, and to contain one molecule of water of crystallization. To this compound, which Baeyer called "*monoresorcinphthalein,*" he assigned the formula $C_6H_3(OH)_2.CO.C_6H_4.COOH$. He found that monoresorcinphthalein, when fused with resorcinol, or even when heated alone above its melting point, gave fluorescein. In the latter case the reaction seemed to proceed according to the following equation:

$$\underset{\text{Monoresorcin-phthalein.}}{2C_{14}H_{10}O_5} = \underset{\text{Fluorescein.}}{C_{20}H_{12}O_5} + \underset{\text{Phthalic anhydride.}}{C_8H_4O_3} + 2H_2O$$

Dihydroxybenzoylbenzoic acid was also made by Liebig[2] in his investigation of resorcinbenzein and fluorescein. His method of preparation was the same as that of Baeyer, while his method of purification differed somewhat. His purified acid contained one and a half molecules of water of crystallization, and melted at 210–211°. He also prepared a diacetyl derivative, having a melting point of 136°. According to Liebig,[3] when fluorescein is made by fusing dihydroxybenzoylbenzoic acid, two modifications are obtained, one red and the other yellow.

R. Meyer and Conzetti[4] obtained dihydroxybenzoylbenzoic acid, along with other products, by the fusion of fluorescein chloride with sodium hydroxide. They give its melting point as about 200°.

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[1] *Ann.*, **183**, 23 (1876).

[2] *J. prakt. Chem.*, **85**, 261 (1912).

[3] *Ibid.*, **85**, 113 (1912).

[4] *Ber.*, **30**, 970 (1897).

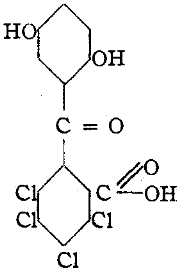
Dibromodihydroxybenzoylbenzoic acid was prepared by Baeyer[1] by heating one part of the potassium salt of tetrabromofluorescein with 20 parts of 50% sodium hydroxide solution to 140°. The same product was obtained by Heller[2] by the bromination of dihydroxybenzoylbenzoic acid in glacial acetic acid solution.

Quenda[3] prepared the methylether acid,

$$CH_3O.C_6H_3(OH).CO.C_6H_4.COOH,$$

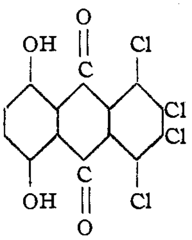
by heating phthalic anhydride, resorcinoldimethylether, and aluminum chloride. Diethoxybenzoylbenzoic acid has also been prepared[4] by this method.

Hövermann[5] made dihydroxybenzoyltetrachlorobenzoic acid,



by heating 3 parts of tetrachlorophthalic anhydride with 7 parts of boric acid to 195°, adding gradually, with stirring, 1.5 parts of hydroquinone and letting the temperature rise to 230°, where it was held for two hours. The mass was boiled with water to remove the boric acid, the residue dissolved in sodium hydroxide solution and the alkaline solution acidified. On long standing, the dihydroxybenzoyltetrachlorobenzoic acid separated in lemon-yellow needles. This was crystallized from xylene. M. p. 231°. The purified acid dissolved in alkalies with orange-red color.

Hövermann obtained tetrachloroquinizarin (contrary to the Höchster Farbwerke patent 172,105),



by heating the above acid with conc. sulfuric acid.

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[1] *Ann.*, 183, 56 (1876).

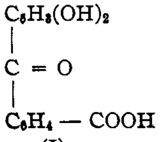
[2] *Ber.*, 28, 315 (1895).

[3] *Gazz. chim. ital.*, 20, 128 (1890).

[4] *Ber.*, 28, 29 (1895).

[5] *Ibid.*, 47, 1210 (1914).

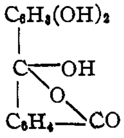
Graebe, Kohn and Huguenin[1] studied monoresorcinphthalein with a view to determining its structure. They considered two formulas:



$$\begin{array}{l} C_6H_3(OH)_2 \\ \vert \\ C = O \\ \vert \\ C_6H_4 - COOH \end{array}$$

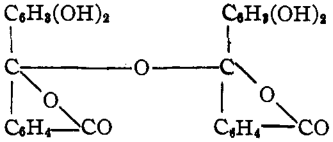
(I).

and

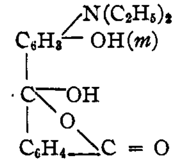


(II).

They conclude that monoresorcinphthalein is best represented by Formula (II), giving as reasons for their choice: It better explains the formaiton of monoresorcinphthalein, as well as the ease with which it goes over into fluorescein. It was found impossible to transform monoresorcinphthalein into a derivative of anthraquinone, whereas benzoylbenzoic acid, under the influence of dehydrating agents, easily gives anthraquinone itself. Finally, monoresorcinphthalein treated with acetyl chloride is converted into an acetyl derivative, which, heated with sodium hydroxide, yields a compound possessing the following constitution:



They state that rhodamine, when fused with sodium hydroxide, is decomposed in the same manner as fluorescein and yields diethylamino-*m*-hydroxybenzoylbenzoic acid,



whereas tetrachlorofluorescein, obtained from tetrachlorophthalic acid, gives dihydroxydichlorofluorescein.

With regard to the positions of the hydroxyl groups in dihydroxybenzoylbenzoic acid, Graebe[2] claims that both stand in the ortho positions with respect to the carbonyl group, as he was unable to transform dihydroxybenzoylbenzoic acid itself, the monoethylether, of the acid,

$$COOH.C_6H_4.CO.C_6H_3(OH).OC_2H_5,$$

or the diethylether,

$$COOH.C_6H_4.CO.C_6H_3(OC_2H_5)_2,$$

into anthraquinone derivatives. In the same year, however, Heller[3] found that the dibromo derivative of dihydroxybenzoylbenzoic acid, ob-

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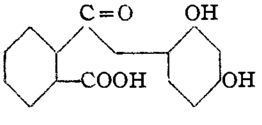
[1] *Arch. sci. phys. nat.*, **2**, 91 (1893).

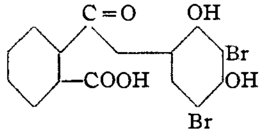
[2] *Ber.*, **28**, 28 (1895).

[3] *Ibid.*, **28**, 315 (1895).

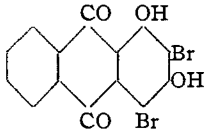
tained by the direct bromination of this acid, was identical with the product obtained by Baeyer[1] by heating eosin with concentrated sodium hydroxide solution. Furthermore, he found that this substance, when heated for two hours with fuming sulfuric acid, containing 20% of the anhydride, was condensed to the same dibromoxanthopurpurin as had been obtained by Plath[2] upon direct bromination of xanthopurpurin. Therefore, having accomplished for the first time the transformation of a decomposition product of fluorescein into a derivative of anthraquinone, Heller thinks that the question of the position of the second hydroxyl group in these compounds is settled in such a manner as to exclude the fluorescein formula proposed by Graebe,[3] and at the same time, the positions of the halogens in dibromodihydroxybenzoylbenzoic acid are determined. He proposes the following formulas:



Dihydroxybenzoylbenzoic acid (monoresorcinphthalein).

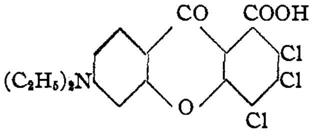


Dibromodihydroxybenzoylbenzoic acid.



Dibromoxanthopurpurin.

Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid has been made in this laboratory by Orndorff and Rose,[4] by the fusion of diethyl-*m*-amino phenol with tetrachlorophthalic acid anhydride, and subsequent decomposition of the condensation product with acid or alkali. They find that hydrochloric acid is removed from the tetrachloro acid even by such weak alkalies as ammonium hydroxide and sodium carbonate, giving rise to a xanthone derivative, 2,3,4-trichloro-6-diethylaminoxanthone-1-carboxylic acid:



As it is highly probable that diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid is an intermediate product in the formation of tetrachlororhodamine,[5] so it also seems likely that dihydroxybenzoyltetrachlorobenzoic acid is an intermediate product in the formation of tetrachlorofluorescein. This investigation was undertaken, therefore, to determine the best method of making dihydroxybenzoyltetrachlorobenzoic acid, to study its properties and characteristic reactions, to prepare and

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[1] *Ann.*, 183, 56 (1876).

[2] *Ber.*, 9, 1205 (1876).

[3] *Ber.*, 28, 30 (1895).

[4] THIS JOURNAL, 38, 2106 (1916).

[5] *Bull. soc. chim.*, 25, 747 (1901).

study some of its derivatives, and to determine, if possible, its role in the formation of tetrachlorofluorescein.

Experimental.

All chlorine determinations given in the following pages were made by the line method.[1] The melting points are uncorrected, and were made in an electrically heated Thiele apparatus, the heat being so regulated as to give a rise in temperature of 1° in 3 seconds. The thermometer used was carefully calibrated against a standard thermometer. For bringing substances to constant weight by means of heat, an electrically heated tube[2] was employed.

The resorcinol used in this investigation was purified by distillation in a partial vacuum. The product was pure white and melted at 109–110°[3] to a clear, colorless liquid, and was completely soluble in water, forming a coloress solution.

The tetrachlorophthalic acid was a commercial product purified by the method of Delbridge,[4] with the following modification: The dark red alkaline solution was boiled with and filtered through boneblack on a plaited hardened filter. This treatment of the alkaline solution was repeated and yielded a solution which was of slight amber color. The tetrachlorophthalic acid obtained from this solution by acidification with hydrochloric acid, had a scarcely perceptible cream color and was pure tetrachlorophthalic acid, as shown by the following analysis:

Subst.: 0.3764; cc. 0.1 *N* $AgNO_3$, 48.08.

Calc. for $C_8H_2O_4Cl_4.{}^1/_2H_2O$: Cl, 45.33. Found: Cl, 45.29.

Part of this acid was converted into tetrachlorophthalic anhydride by heating in a water oven at about 100° for 120 hours.[5]

Preparation of Dihydroxybenzoyltetrachloro-*o*-benzoic Acid.—In order that the best conditions for making this acid might be ascertained, numerous condensations were carried out. The proportion of resorcinol to tetrachlorophthalic acid was varied from one-tenth of one molecular weight each up to as high as 3 parts by weight of resorcinol to 1 part of tetrachlorophthalic acid. The temperature at which the condensations were carried out varied from 100 to 190° and the time of heating from 2 to 36 hours. Within these limits of temperature and time of heating, and with all the above proportions of resorcinol to tetrachlorophthalic acid some dihydroxybenzoyltetrachloro-*o*-benzoic acid was formed together with more or less tetrachlorofluorescein. In no case was all the

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[1] *Am. Chem. J.*, **41**, 397 (1909).

[2] *Ibid.*, **48**, 477 (1912).

[3] P. Lemaire, *Bull. soc. pharm.* (de Bordeaux), **50**, 110.

[4] *Am. Chem. J.*, **41**, 414 (1909).

[5] *Ibid.*, **41**, 359 (1909).

tetrachlorophthalic acid used up. Similar results were obtained with tetrachlorophthalic anhydride.

Attempts were made to bring about the condensation in the presence of an indifferent solvent, both toluene and xylene being used. The results were similar to those where fusion was employed, except that the proportion of tetrachlorofluorescein was apparently much larger, and especially was this the case with xylene as solvent.

One condensation was attempted in the presence of water. Three g. of resorcinol, 10 g. of tetrachlorophthalic acid, and 20 g. of water were placed in a hard glass tube, the tube sealed by heat, and the mixture heated in a bomb furnace at 165–179° for 36 hours. This experiment resulted in the formation of a small amount of tetrachlorofluorescein, but not enough dihydroxybenzoyltetrachloro-*o*-benzoic acid was formed for separation and identification.

The following method of preparation was found to give the most satisfactory results: 50 g. of tetrachlorophthalic acid and 40 g. of resorcinol were heated in a 250 cc. round bottom flask for 12 to 15 hours, in a Victor Meyer air bath containing boiling xylene. The temperature inside the flask never exceeded 131°. After the heating had been continued for about an hour the mixture became plastic and of a light yellow color. Water was driven out of the flask as the tetrachlorophthalic acid was converted into the anhydride. At this point, and at frequent intervals thereafter, the contents of the flask were thoroughly stirred. A dark amber-colored syrup gradually formed until almost all of the contents of the flask became liquid. The syrup began to thicken after about 8 hours, and at the end of 12 hours the fused mass consisted of a small amount of the syrup and a large amount of more or less granular material. This fused material was poured into a liter of cold water and thoroughly stirred until all the granular particles had been disintegrated. To the light yellow suspension was added 3 cc. of conc. hydrochloric acid and the stirring continued until the emulsion was broken down and a light yellow flocculent material began to settle out. After two hours, standing, the supernatant liquid was decanted off, distilled water added, and after thorough stirring the residue was filtered on a Büchner funnel and washed until free from resorcinol and acid. This residue was taken up in a *cold* 2% sodium hydroxide solution.[1] By this treatment the dihydroxybenzoyltetrachloro-*o*-benzoic acid, together with a small amount of tetrachlorofluorescein formed in the condensation, went into solution, leaving undissolved all of the unchanged tetrachlorophthalic anhydride. This was found to be equivalent to 4.9 g. of tetrachlorophthalic acid, or 9.8% of tetrachloro-

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[1] It was found that this strength of alkali did not split off hydrochloric acid from the dihydroxy acid (p. 1246).

phthalic acid taken in the beginning. This represents a yield of about 90% of the tetrachloro acid.

The alkaline solution of dihydroxybenzoyltetrachloro-*o*-benzoic acid was made strongly acid by the addition of hydrochloric acid. Steam was passed into the acid solution, whereupon the dihydroxy acid which separated at first in flocks was rendered granular, and consequently more easily filtered. It was filtered off with the aid of suction, washed with water until free from hydrochloric acid and chlorides, and dried in the water oven. The dried material was orange-yellow, and melted at 225–230°. It was purified by conversion into the acetate, hydrolyzing the pure acetate with cold, conc. sulfuric acid and recrystallization from water or dilute alcohol (p. 1242).

Dihydroxybenzoyltetrachloro-*o*-benzoic acid prepared in this way is *colorless* and losses two molecules of water when dried to constant weight in an evacuated desiccator at room temperature over sulfuric acid, as shown by the following results:

Subst.: I, 1.1566; II, 0.2054. Loss: I, 0.0942; II, 0.0171.

Calc. for $C_{14}H_6O_5Cl_4.2H_2O$: H_2O, 8.34. Found: H_2O, I, 8.14; II, 8.32.

This dried material was heated for 12 hours at 130–150° without further loss in weight.

Chlorine determinations on this material dried to constant weight gave the following results:

Subst.: I, 0.1544; II, 0.2973. Cc. 0.1 *N* $AgNO_3$; I, 15.60; II, 29.99.

Calc. for $C_{14}H_6Cl_4O_5$: Cl, 35.82. Found: Cl, I, 35.83; II, 35.77.

Pure dihydroxybenzoyltetrachloro-*o*-benzoic acid melts at 227°, and is at the same time decomposed into tetrachlorophthalic acid anhydride and tetrachlorofluorescein. This tetrachlorofluorescein is the same as that obtained by Orndorff and Hitch[1] by condensing resorcinol with tetrachlorophthalic acid, since it gives an acetate which melts at 256°[2] and has all the other properties of tetrachlorofluorescein.

The *pure* dihydroxy acid is colorless and dissolves in cold dilute aqueous alkalies without color, and is precipitated from these solution as an amorphous white solid upon acidification. It dissolves in a very large volume of boiling water, from which it separates, upon cooling, in long fibrous needles. Cold concd. sulfuric acid dissolves it, forming a garnet-red solution. If this solution is heated below 94° a compound is formed which dissolves in aqueous alkalies with a deep red color, and is precipitated from the alkaline solution by acids as a light yellow finely divided precipitate.

If the acid solution is heated above this temperature tetrachlorophthalicanhydride is split off. When alkaline solutions of dihydroxybenzoyl-

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[1] THIS JOURNAL, 36, 685 (1914).

[2] *Ibid.*, 36, 692 (1914).

tetrachloro-*o*-benzoic acid are boiled, hydrochloric acid is split off. This takes place more readily in alcoholic alkali solutions than in aqueous alkalies (p. 1246). The dihydroxybenzoyltetrachloro-*o*-benzoic acid is easily soluble in alcohol, methyl alcohol, ether, ethyl acetate and glacial acetic acid, and difficulty soluble in hot benzene, toluene or xylene. It is only very slightly soluble in water. When pure it crystallizes readily from 50% alcohol, forming thin, colorless needles.

The Triacetate of Dihydroxybenzoyltetrachloro-*o*-benzoic Acid.—One part of the cruse dihydroxybenzoyltetrachloro-*o*-benzoic acid and 5 parts of acetic anhydride were heated until solution of the acid was complete, and the solution then boiled for one-half hour. The acetic anhydride was distilled off until crystals began to form, when distillation was discontinued, and the contents of the flask rapidly cooled. The almost colorless crystals which formed were filtered off by means of a Büchner funnel, and washed with a small volume of acetic anhydride and then with ether until no odor of acetic anhydride remained. The crystals were rendered colorless by this treatment. This product was dissolved in benzene, part of the solvent distilled off, and the remaining solution cooled rapidly while being strongly agitated. After some time, colorless crystals began to separate from the solution, and, finally, the entire contents of the flask became almost solid. The residual benzene was filtered off by means of suction and the crystals washed with benzene and air-dried. This air-dried material lost no weight when heated in the electric drying tube,[1] at 110°. The melting point of the product, dried at 110°, is 166–167°, and is not changed when the triacetate is crystallized from absolute ethyl alcohol or from methyl alcohol.

Determinations of chlorine on the product, heated to constant weight, at 110°, show that the compound is the triacetate of dihydroxybenzoyltetrachloro-*o*-benzoic acid.

Subst.: I, 0.2010; II, 0.2027. Cc. 0.1 *N* $AgNO_3$, I, 15.38; II, 15.52.

Calc. for $C_{14}H_8Cl_4O_5(CH_3CO)_3$: Cl, 27.17. Found: Cl, I, 27.14; II, 27.15.

The triacetate of dihydroxybenzoyltetrachloro-*o*-benzoic acid is very soluble in acetone, easily soluble in benzene, ethyl acetate, glacial acetic acid, and difficultly soluble in ethyl alcohol and in methyl alcohol. When this triacetate is treated with cold dilute alkalies, it saponifies very slowly. When treated with alcoholic potassium hydroxide solution, it dissolves with a yellow color and a very slight greenish fluorescence. When this alcoholic solution of the triacetate is diluted and acidified with sulfuric acid, a milk-white emulsion is formed, which may be coagulated by adding more acid and stirring, or by boiling with a current of steam. This treatment with alcoholic potash splits off hydrochloric acid (p. 1246), as shown by testing the filtrate with silver nitrate solution. The triacetate dis-

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[1] *Am. Chem. J.*, **48**, 477 (1912).

solves in cold conc. sulfuric acid with a garnet-red color. When this solution is poured into a large volume of water, dihydroxybenzoyltetrachloro-*o*-benzoic acid is precipitated. When this precipitate is filtered off with suction and dried it is found to have a slight tinge of yellow, due perhaps to a trace of tetrachlorofluorescein.

Monosodium Salt.—Ten g. of dihydroxybenzoyltetrachloro-*o*-benzoic acid was dissolved in an excess of cold 2% sodium hydroxide solution, and dil. hydrochloric acid (1 : 8) added until the solution was only slightly alkaline. The light yellow sodium salt which separated out was filtered off with suction, washed with a small volume of water, and finally crystallized from 95% alcohol. The dried material melts with decomposition at about 295°. From alcohol the sodium salt crystallizes in well-defined crystals having only a slight gray color. The crystalline material is fairly easily soluble in hot water but dissolves rather slowly in cold water. When the water solution is acidified with hydrochloric acid, dihydroxybenzoyltetrachloro-*o*-benzoic acid is precipitated.

The product obtained by crystallization from alcohol contains two molecules of water of crystallization, as shown by the following analysis made on the air-dried material:

Subst.: 2.0857. Loss, H_2O at 180°, 0.1552.

Calc. for $C_{14}H_5Cl_4O_5Na.2H_2O$: H_2O, 7.93. Found: H_2O, 7.44.

A chlorine determination on the material dried to constant weight gave the following result:

Subst.: 0.4469. Cc. 0.1 *N* $AgNO_3$, 42.72.

Calc. for $C_{14}H_5Cl_4O_5Na$: Cl, 33.94. Found: Cl, 33.90.

An analysis for sodium was made as follows: A weighed amount of the dried sodium salt was dissolved in water, the solution brought to boiling, and a measured excess of standard sulfuric acid added. The dihydroxy acid which separated was filtered off and washed with distilled water. The excess of sulfuric acid in the filtrate was titrated with standard sodium hydroxide solution, using phenoltetrachlorophthalein as indicator. The result of this analysis follows:

Subst.: 0.4786. Cc. 0.1 *N* H_2SO_4, 11.06.

Calc. for $C_{14}H_5Cl_4O_5Na$: Na, 5.50. Found: Na, 5.33.

Action of Dry Ammonia Gas on the Tetrachloro Acid.—When dry ammonia gas is passed over dry dihydroxybenzoyltetrachloro-*o*-benzoyl acid it is absorbed very rapidly, and an appreciable amount of heat is evolved. The material assumes a scarcely perceptible yellow color. The dihydroxy acid exhibits toward ammonia an abnormal absorptive power, since it takes up more than 3 and less than 4 molecules of ammonia. On standing in an evacuated Hempel desiccator containing conc. sulfuric acid the material comes to constant weight when only one molecule of ammonia remains.

The following results were obtained:

	I.	II.	III.
Substance	0.2649	0.5340	0.5927
Weight of salt	0.3026	0.6107	0.6762

Calc. for $C_{14}H_6Cl_4O_5.(NH_3)_3$: NH_3, 11.43
Calc. for $C_{14}H_6Cl_4O_5.(NH_3)_4$: NH_3, 14.68
Found: I, 12.46; II, 12.56; III, 12.35

For Sample III brought to constant weight in an evacuated desiccator:

Subst.: 0.5927. Weight of salt, 0.6183.
Calc. for $C_{14}H_6Cl_4O_5.(NH_3)$: NH_3, 4.12. Found: NH_3, 4.14.

The Action of Hydroxylamine on the Tetrachloro Acid.—Five g of dihydroxybenzoyltetrachloro-*o*-benzoic acid was dissolved in ethyl alcohol and 0.9 g. hydroxylaminehydrochloride, dissolved in 3 cc. of water, was added to this solution. The calculated amount (0.32 g.) of sodium necessary to neutralize the hydrochloric acid of the hydrochloride, was dissolved in absolute alcohol and the two solutions poured together. Upon boiling the resulting solution a light yellow, finely crystalline substance separated out of the solution. This product was filtered off, washed with a small volume of alcohol and then with water, and was finally recrystallized from absolute alcohol. The light yellow crystals which separate from the alcoholic solution begin to darken when heated to 230° and melt with decomposition at 254°. Upon standing in conc. hydrochloric acid hydroxylamine is split off and the dihydroxybenzoyltetrachloro-*o*-benzoic acid is reformed.

That the product formed above is the hydroxyl-ammonium salt of dihydroxybenzoyltetrachloro-*o*-benzoic acid and not the oxime is shown by the following halogen determination on the material dried to constant weight at 110°:

Subst.: 0.2470. Cc. 0.1 *N* $AgNO_3$, 22.89.
Calc. for $C_{14}H_5O_5Cl_4.NH_3OH$: Cl, 33.06. Found: Cl, 32.86.
Calc. for the oxime of dihydroxybenzoyltetrachloro-*o*-benzoic acid, $C_{14}H_6O_4Cl_4$.-OH: Cl. 34.51.

3,5-Dibromo-2,4-dihydroxybenzoyltetrachloro-*o*-benzoic Acid.—One part, by weight, of dihydroxybenzoyltetrachloro-*o*-benzoic acid was dissolved in 6 parts of hot glacial acetic acid, and to the cooled solution 5% in excess of two molecules of bromine to one of the dihydroxy acid was added, and the mixture allowed to stand overnight. The light yellow crystalline product was filtered off on a Büchner funnel, washed with a small volume of glacial acetic acid, then with 80% acetic acid, and finally with water. The crystalline residue was dissolved in 95% alcohol and water added until a precipitate formed. The mixture was then heated until a clear yellow solution resulted, which was allowed to cool slowly. The dibromo compound crystallized in fine yellow needles which melted at 210–212°. This product was crystallized from glacial acetic acid. The dried crystals from this recrystallization melted at 211–212°. These crystals contain one molecule of acetic acid of crystallization, as shown by the following result:

Subst.: 0.9325. Loss, H_3CCOOH, 0.0935.

Calc. for $C_{14}H_4Cl_4O_5Br_2.H_3CCOOH$: H_3CCOOH, 9.78. Found: 10.03.

That the product is pure dibromodihydroxybenzoyltetrachloro-*o*-benzoic acid is shown by the following halogen determinations on the material dried to constant weight at 150°.

	I.	II.
Substance, g	0.4410	0.3727
Silver halides, g	0.7557	0.6328
0.1 *N* silver nitrate, cc	47.86	40.11
Bromine, %	28.40	27.91
Chlorine, %	25.88	25.78

Calc. for $C_{14}H_4O_5Cl_4Br_2$: Br, 28.87; Cl, 25.61.

This dibromo compound dissolves in alkalies with a yellow color, and is precipitated from the alkaline solution by addition of acids, as a light yellow flocculent precipitate.[1] Conc. sulfuric acid dissolves the dibromo compound with a rich garnet color.

When this dibromo compound is heated to its melting point tetrachlorophthalic anhydride is split off and tetrachloroeosin is formed.

The dibromo acid is very soluble in ethyl alcohol, methyl alcohol and acetone, easily soluble in hot glacial acetic acid, and, in benzene, it is much more readily soluble than the corresponding dihydroxy acid.

The acid obtained by the saponification of its acetate with sulfuric acid also melts at 211–212° and is nearly colorless.

The Action of Dry Ammonia Gas on the Dibromo Acid.—When dry ammonia gas is passed over the dibromo derivative it is absorbed very rapidly at first. Much heat is evolved and the material, which increases some what in volume, assumes a bright yellow color. Approximately 4 molecules of ammonia are absorbed as shown by the following results:

Subst.: 0.9385. Gain, NH_3, 0.0988.

Calc. for $C_{14}H_4Cl_4O_5Br_2.(NH_3)_4$: NH_3, 10.95. Found: NH_3, 10.53.

When heated to constant weight at 60° in a current of dry air the tetrammonia compound loses two molecules of ammonia, yielding a stable diammonium salt:

Subst.: 0.8397. Gain, NH_3, 0.0496.

Calc. for $C_{14}H_4Cl_4O_5Br_2.(NH_3)_2$: NH_3, 5.79. Found: NH_3, 5.58.

The diammonium salt is less highly colored than the compound with 4 molecules of ammonia.

Triacetate of 3,5-Dibromodihydroxybenzoyltetrachloro-*o*-benzoic Acid.—One part, by weight, of dibromodihydroxybenzoyltetrachloro-*o*-benzoic

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[1] When perfectly pure the acid is colorless and dissolves in alkalies without color.

acid was dissolved in 5 parts of acetic anhydride and the solution boiled for a quarter hour. Two-thirds of the solvent was distilled off and the flask containing the residue was rapidly cooled while being strongly agitated. The triacetate separated in fine white crystals. This product was filtered off with suction, washed with a small volume of acetic anhydride, and then with ether until no odor of acetic anhydride remained. The pure white crystalline material was recrystallized from absolute alcohol. This material loses no appreciable weight when dried at 150°, and melts sharply at 204.5°.

Analyses on the dried material gave the following results:

	I.	II.
Substance, g	0.3770	0.4361
Silver halides, g	0.5268	0.5941
0.1 *N* silver nitrate, cc	33.38	37.55
Chlorine, %	21.17	20.79
Bromine, %	23.03	23.57

Calc. for $C_{14}HCl_4Br_2O_5(COCH_3)_3$: Cl, 20.86; Br, 23.51.

The triacetate dissolves in conc. sulfuric acid with a deep garnet color, undergoing saponification and forming the dibromodihydroxy acid. This is precipitated on pouring the solution into a large volume of water in the form of white flocks. When this material is recrystallized from dilute alcohol, if gives practically colorless crystals of the pure dibromodihydroxy acid, having a melting point of 211–212°.

2,3,4-Trichloro-6-hydroxyxanthone-1-carboxylic Acid.

Ten g. of the triacetate of the tetrachloro acid were suspended in 300 cc. of 5% alcoholic caustic potash solution and allowed to stand for 3 hours with occasional shaking. The triacetate dissolved, yielding a solution having a yellow color with a greenish fluorescence. This solution was poured into a liter of water and dil. sulfuric acid added. The contents of the flask were boiled, by passing in steam, until nearly all of the alcohol had been boiled off. This gave a voluminous flocculent white precipitate, which was filtered off and washed with water until free from sulfuric acid. The filtrate was tested with silver nitrate solution and showed the presence of hydrochloric acid. The residue was crystallized from dilute alcohol, yielding pure white fibrous needles. This material, when dry, melted at 279–280°.

The same product was obtained by boiling dihydroxybenzoyltetrachloro-*o*-benzoic acid with 5% aqueous sodium hydroxide solution, precipitating with hydrochloric acid, and subsequently crystallizing from dilute alcohol.

This compound was made on a larger scale as follows: The crude triacetate of dihydroxybenzoyltetrachlorobenzoic acid was dissolved in 5% alcoholic sodium hydroxide solution and all the alcohol distilled off on the water bath. A volume of water, sufficient to dissolve the sodium salts which had formed, was added and the mixture heated on the water bath until solution was complete. Then 50% sodium hydroxide solution was added until a precipitate began to form in the boiling solution. Heating was discontinued and in a few minutes the mass solidified. This was thrown on a hardened filter and suction applied. The alkaline filtrate was strongly fluorescent, due to the presence of tetrachlorofluorescein. The gelatinous residue was washed with absolute alcohol until the filtrate ran through almost free from fluorescence, then water was poured into the funnel containing the residue. The sodium salt being very easily soluble in water, soon dissolved and a light yellow solution was obtained. Upon adding hydrochloric acid to this solution a milky white precipitate was thrown down. This was filtered off, washed with water, and dissolved in 95% alcohol, from which it crystallized in snow-white needles. More 50% sodium hydroxide solution was added to the fluorescent filtrate, which was allowed to stand overnight. Beautiful light yellow needles of the sodium salt separated from the solution. These were filtered off, washed with absolute alcohol, and air-dried. Water was added to the acidified alcoholic filtrate and the free acid remaining separated out as a gelatinous precipitate. The mixture was heated on the water bath until all solid material was again in solution, after which the solution was allowed to cool slowly. A voluminous crop of white crystals was obtained in this way. When filtered with suction these crystals formed a felted mass which very closely resembles filter paper in appearance. This material was recrystallized from methyl alcohol, benzene, and glacial acetic acid in an attempt to get a product which had a sharp melting point, but such a product could not be obtained. The substance crystallized from each of these solvents begins to shrink at 230° and then changes but little until the temperature reaches 279°, at which temperature it begins to swell, bubbles are formed and the material which finally remains in a liquid state is of a reddish brown color.

The trichloro acid crystallizes from dilute alcohol with two molecules of water of crystallization, one-half molecule of which is lost upon drying in a Hempel desiccator containing conc. sulfuric acid. This is shown by the following data:

Subst.: 0.5725. Loss, 0.0136.
Calc. for $C_{14}H_5O_5Cl_3.2H_2O-0.5H_2O$: Loss for 0.5 H_2O, 2.28. Found: 2.38.

A chlorine determination on the material dried as above gave the following result:

Subst.: 0.2402. Cc. 0.1 *N* $AgNO_3$, 18.76.
Calc. for $C_{14}H_5O_5Cl_3.1.5H_2O$: Cl, 27.52. Found: 27.70.

Chlorine determinations on the air-dried material gave the following results:

Subst.: I, 0.1717; II, 0.1787. Cc. 0.1 *N* $AgNO_3$, I, 13.00; II, 13.55.
Calc. for $C_{14}H_5O_5Cl_3.2H_2O$: Cl, 26.90. Found: Cl, I, 26.84; II, 26.89.

Chlorine determinations on the material dried to constant weight at 130° gave the following results:

Subst.: I, 0.2355; II, 0.2765. Cc. 0.1 *N* $AgNO_3$, I, 19.59; II, 22.93.
Calc. for $C_{14}H_5O_5Cl_3$: Cl, 29.59. Found: Cl, I, 29.50; II, 29.41.

Several attempts were made to prepare an oxime of the trichloro acid, but none of these was successful.

The trichloro acid dissolves in conc. sulfuric acid with a yellow color, showing a greenish fluorescence, and is precipitated from this solution as a white flocculent mass upon the addition of a large volume of water.

Acetate of the Trichloro Acid.—One part, by weight, of the trichloro acid and 4 parts of acetic anhydride were heated at the boiling point of the solution for 15 minutes. The hot solution was filtered. by the aid of suction, and the filtrate cooled rapidly in running water. The white needle crystals which separated were filtered off when the mixture had become cold. They were dissolved in absolute alcohol, part of the solvent distilled off and the solution allowed to cool slowly. The acetate crystallized out in beautiful white prisms. This material was then crystallized from methyl alcohol, which yielded white fibrous needles. Part of the material from methyl alcohol was crystallized from benzene, which yielded thin prisms.

The product from methyl alcohol and also that from benzene, decomposes when heated in a sealed tube to 220–221°. The substance first contracts into a globule which then swells up and forms bubbles as if a gas were being driven off.

The following chlorine determinations on the compounds, dried to constant weight at 130–140°, show it to be the monoacetate of the trichloric acid.

Subst.: I, 0.2269; II, 0.2704. Cc. 0.1 *N* $AgNO_3$, I, 16.99; II, 20.17.
Calc. for $C_{14}H_4O_5Cl_3.COCH_3$: Cl, 26.50. Found: Cl, I, 26.55; II, 26.46.

The acetate of the trichloro acid is not very soluble in absolute alcohol, less soluble in methyl alcohol, and very soluble in benzene.

It dissolves in conc. sulfuric acid, giving a pale yellow color and a slight greenish fluorescence. When this solution is poured into a large volume of cold water, the trichloro acid is thrown down as an almost gelatinous white precipitate. This is, probably, the hydrate.

The acetate of the trichloro acid is only partially saponified with aqueous alkaline solutions, but, in alcoholic alkaline solutions, it saponifies readily, even in the cold, giving a light yellow solution with greenish fluorescence.

Action of Dry Ammonia Gas on the Trichloro Acid.—When dry ammonia gas is led over a weighed portion of the trichloro acid, which has been dried to constant weight, the material assumes a bright yellow color and increases in weight, rapidly at first, then more slowly until the substance comes to constant weight. The trichloro acid exhibits an abnormal absorbing power toward ammonia, since it takes up more than one molecule and less than two. This is shown by the following result:

Subst.: 0.3957. Final weight, 0.4183. Gain, 0.0226.
Calc. for $C_{14}H_5O_5Cl_3.NH_3$: NH_3, 4.52. Found: 5.40.
Calc. for $C_{14}H_5O_5Cl_3.(NH_3)_2$: NH_3, 8.65.

When allowed to stand in an evacuated Hempel desiccator containing conc. sulfuric acid, the substance lost ammonia and came to constant weight when only one molecule of ammonia remained as shown by the following result:

Final weight of above salt, 0.4149: Final gain, 0.0192.
Calc. for $C_{14}H_5O_5Cl_3.NH_3$: NH_3, 4.52. Found: 4.63.

This salt is comparatively stable as it loses weight only very slowly when heated at 150°, turning brown and, apparently, undergoing slight decomposition.

Disodium Salt of the Trichloro Acid.—This salt was made as described in the preparation of the trichloro acid (p. 1246). It was crystallized from alcohol, then from water.

When dihydroxybenzoyltetrachloro-*o*-benzoic acid is boiled with 5% aqueous sodium hydroxide solution, hydrochloric acid is split off (p. 1246) with the formation of the disodium salt of the trichloro salt, which is salted out upon adding a concentrated solution of sodium hydroxide to its solution.

The disodium salt crystallizes in light yellow needles containing water of crystallization.

The following analyses of the dried material show it to be the disodium salt of the trichloro acid. It was dried to constant weight at 130°.

Subst.: I, 0.2490; g. Na_2SO_4, 0.0903; II, 0.3543; cc. 0.1 *N* H_2SO_4, 17.88.
Calc. for $C_{14}H_8Cl_3O_5Na_2$: Na, 11.40. Found: Na, I, 11.74; II, 11.61.

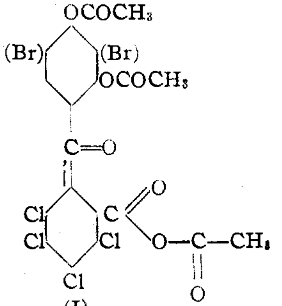
The aqueous and alcoholic solutions of the disodium salt are yellow with greenish fluorescence. From an aqueous solution of this salt the colorless trichloro acid is precipitated upon acidification.

Theoretical.

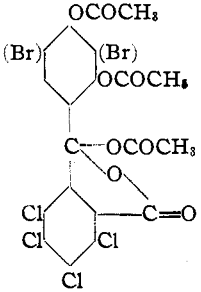
In the preparation of dihydroxybenzoyltetrachoro-*o*-benzoic acid no attempt was made to employ the method used by Baeyer (p. 1235) in the preparation of his "*monoresorcinphthalein.*" In the first place, it was more to the point of this investigation to prepare the dihydroxy acid directly from resorcinol and tetrachlorophthalic acid. In the second place, the work of Graebe, Kohn and Huguenin (p. 1237) would seem to preclude the use of Baeyer's method for the preparation of this acid since, according to these authors, tetrachlorofluorescein when evaporated with a solution of sodium hydroxide reacts in a different manner, and yields dihydroxydichlorofluorescein.

Dihydroxybenzoyltetrachloro-*o*-benzoic acid has been prepared by condensing resorcinol with tetrachlorophthalic acid. The *pure* product is *colorless* and dissolves in alkalies *without color*. The isomeric dihydroxybenzoyltetrachlorobenzoic acid which Hövermann (p. 1236) obtained by condensing hydroquinone with tetrachlorophthalic anhydride, was evidently not a perfectly pure product since it was colored and dissolved in alkalies with an orange-red color. Dihydroxybenzoyl-*o*-benzoic acid is also colorless when *perfectly pure* and as both Baeyer and Liebig describe their product as having a yellow color their acid was also impure.

It is interesting to note that dihydroxybenzoyltetrachloro-*o*-benzoic acid and, likewise, its dibromo derivative, form *tri*acetates when boiled with acetic anhydride, whereas Liebig (p. 1235) obtained from dihydroxybenzoylbenzoic acid what he called a *di*acetate. It seems highly probable from the results of this investigation that Liebig's *di*acetate is really a *tri*acetate. These triacetates are stable compounds, which do not undergo any change when boiled with alcohols,[1] hence they are not mixed anhydrides as shown in Formula I, but must be true acetates, as shown in Formula II:

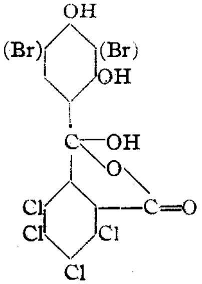


(I).

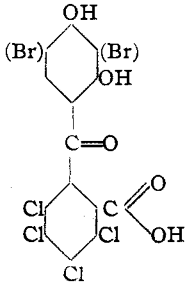


(II).

The formation of a triacetate would indicate that Formula III more nearly represents the constitution of the dihydroxy acids than does Formula IV,



(III).



(IV).

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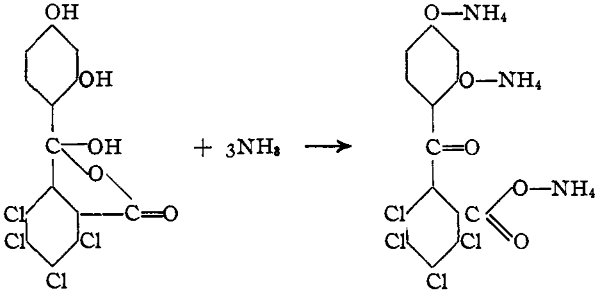
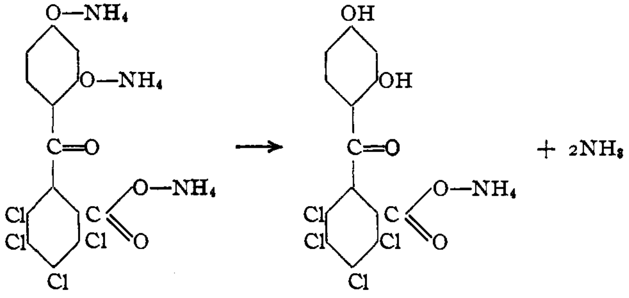
[1] THIS JOURNAL, 38, 2105 (1916).

or that the acids can react in tautomeric forms represented by the above formulas, just as the phthaleins do. The fact that the acids are *colorless* is also an argument in favor of Formula III.

The dihydroxy acid first forms with dry ammonia an unstable, colorless, *tri*ammonium salt, which, by the loss of ammonia, forms the stable *mono*ammonium salt. The reactions are as follows:



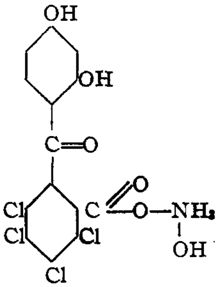
Unstable.



Stable.

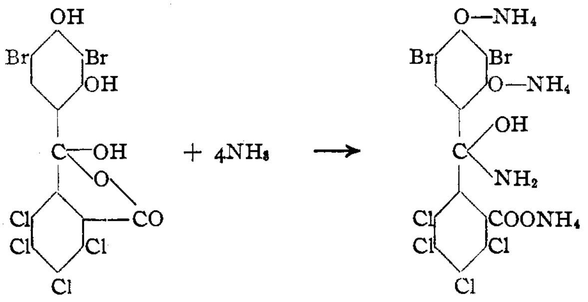
It is highly probable that the excess of ammonia over the 3 molecules (p. 1243) is attached to the carbonyl group. The fact that the acid forms a stable ammonium salt indicates that it acts as a monobasic acid, as is shown in Formula IV (p. 1250).

The product formed by the action of hydroxylamine upon the tetrachloro acid is the hydroxylammonium salt of dihydroxybenzoyltetrachloro-*o*-benzoic acid, and is represented by the following formula:

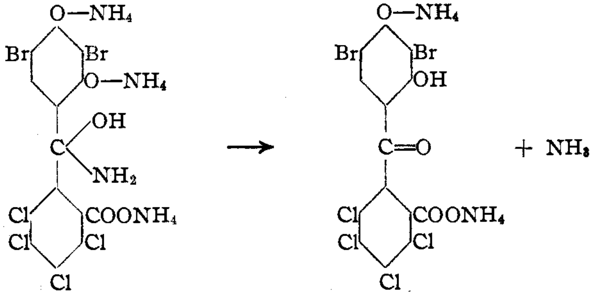


The dibromodihydroxy acid is, as was to be expected, more acid than the dihydroxy acid itself. This is shown by the fact that it absorbs practically *four* molecules of ammonia and loses only *two* when heated to 60° in a current of dry air.

The reactions may be represented as follows:

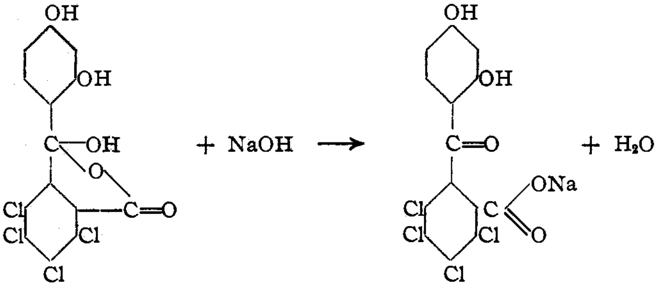


Unstable.

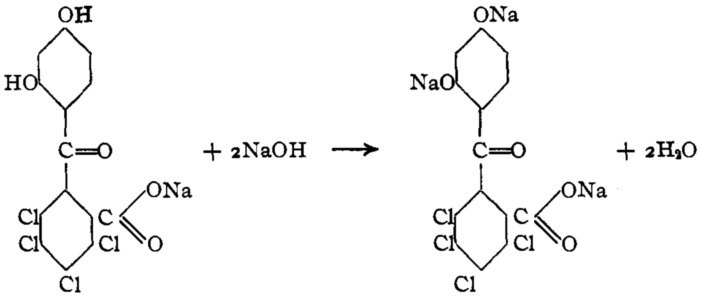


Stable.

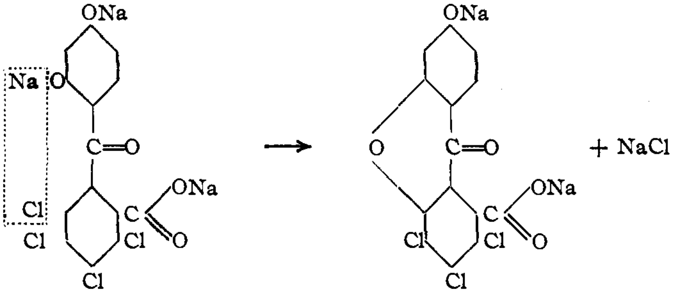
The action of caustic alkalies on the dihydroxy acid is represented by the following reactions:



Monosodium salt of tetrachloro acid.

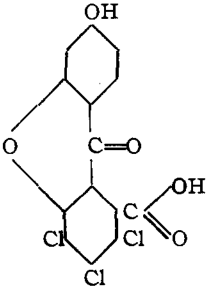


Trisodium salt.

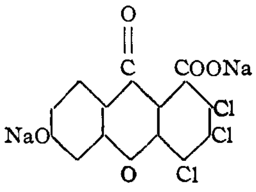


Disodium salt of trichloro acid.

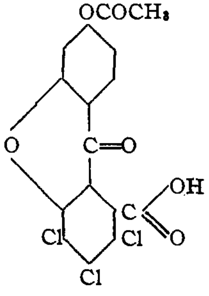
When solutions of the disodium salt of the trichloro acid are acidified the colorless trichloro acid is precipitated. This acid yields a *mono*acetate with acetic anhydride, and a disodium salt with sodium hydroxide. The fact that it forms a *di*sodium salt and a *mono*acetate shows that the acid properties have been increased by the formation of the xanthone ring and that one of the phenol hydroxy groups has taken part in the formation of that ring. The formulas of the acid and its disodium salt and acetate are given below:



2,3,4-Trichloro-6-hydroxy-xanthone-1-carboxylic acid.

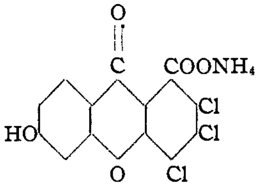


Disodium salt.



Monoacetate of the trichloro acid.

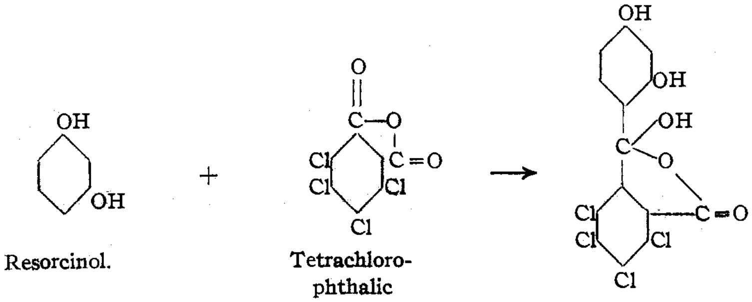
The trichloro acid absorbs more than one molecule and less than two of dry ammonia. The excess of ammonia over one molecule is lost very readily and the stable *mono*ammonium salt results. This salt is yellow like the disodium salt and is represented by the following formula:



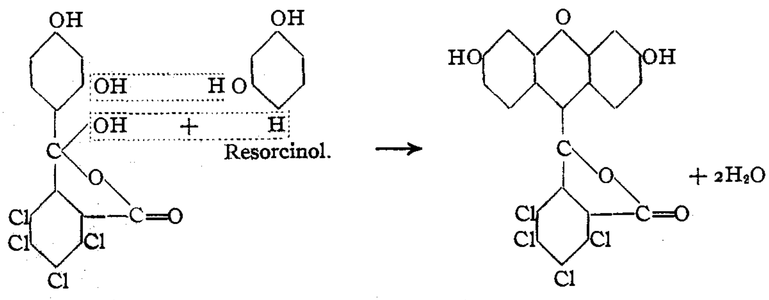
Neither the tetrachloro nor the trichloro acid yields an ester when boiled with methyl alcohol containing 3% of hydrochloric acid gas. This is probably a case of steric retardation or hindrance due to the presence of ortho substituents.

The fact that neither of these acids forms an oxime is in accord with the observations of V. Meyer and Baum[1] that the ortho-substituted ketones do not form oximes.

It has been shown by the results of this investigation that the formation of tetrachlorofluorescein takes place in two steps and that dihydroxybenzoyltetrachloro-*o*-benzoic acid is the intermediate product. According to this view the reactions may be represented as follows:



Resorcinol. Tetrachloro-phthalic anhydride. Dihydroxy acid.



Dihydroxy acid. Tetrachlorofluorescein (lactoid).

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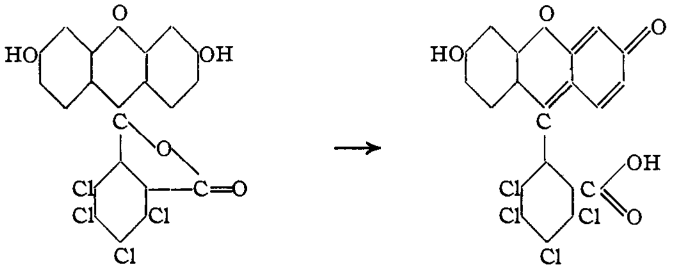
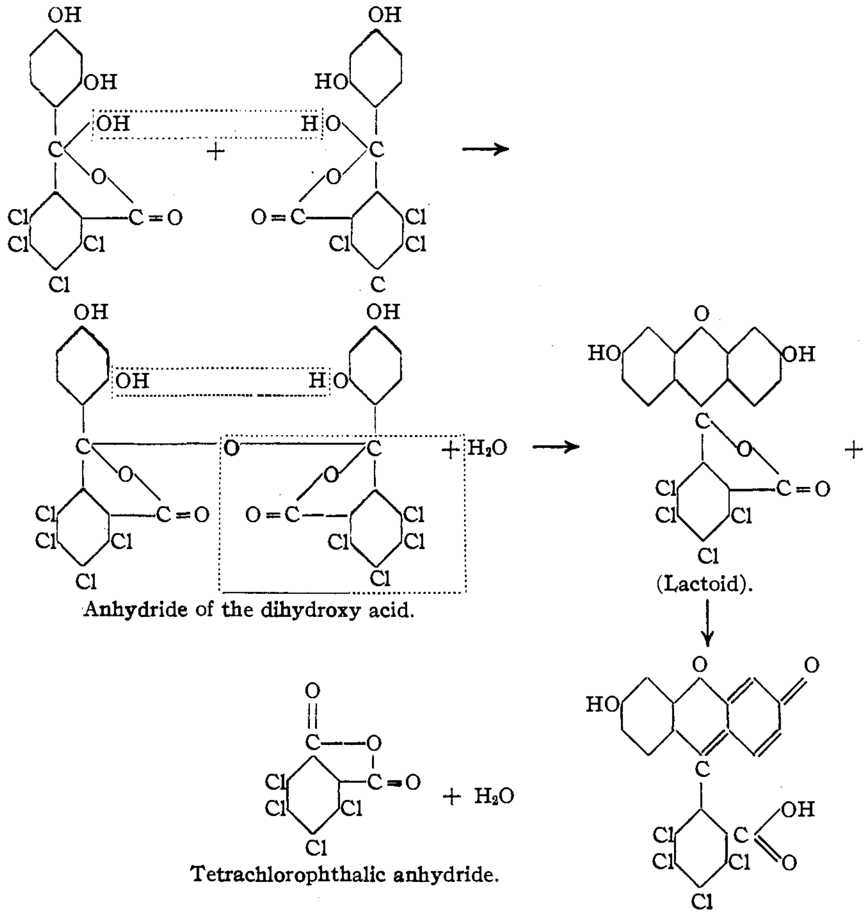
[1] *Ber.*, **28**, 3207 (1895).



Tetrachlorofluorescein (quinoid).

The reaction goes to completion very readily after the intermediate product has been formed. This is made evident by the fact that merely heating the intermediate compound with resorcinol to 110° results in the formation of some tetrachlorofluorescein, and also by the fact that



Anhydride of the dihydroxy acid.

(Lactoid).

Tetrachlorophthalic anhydride.

Tetrachlorofluorescein (quinoid).

in no case could the intermediate product be obtained free from tetrachlorofluorescein by the fusion of resorcinol with tetrachlorophthalic acid or its anhydride.

When dihydroxybenzoyltetrachloro-*o*-benzoic acid is heated to its melting point tetrachlorofluorescein and tetrachlorophthalic anhydride are formed, and the preceding reactions probably take place[1]: The tetrachlorofluorescein formed in this way is identical with that which is formed by the fusion of resorcinol with tetrachlorophthalic anhydride (p. 1241). This is contrary to the result reached by Liebig (p. 1235), who claims that a product is formed when *dihydroxybenzoylbenzoic acid* is heated above its melting point different from ordinary fluorescein. Liebig calls this new product γ-fluorescein.

A similar reaction takes place when the dibromo derivative of the tetrachloro acid is heated above its melting point, and the end products are tetrachloroeosin and tetrachlorophthalic anhydride.

It seems highly probable that phthaleins in general may be prepared in this way, by first preparing the intermediate product corresponding to dihydroxybenzoyltetrachloro-*o*-benzoic acid and then heating this intermediate product above its melting point. Phenolphthalein, fluorescein, eosin, tetrachlorofluorescein and tetrachloroeosin have already been prepared in this way.

Summary.

A brief statement of the results of this investigation follows:

1. Dihydroxybenzoyltetrachloro-*o*-benzoic acid has been prepared by fusing resorcinol with tetrachlorophthalic acid.

2. The dihydroxy acid has been converted into tetrachlorofluorescein by heating it above its melting point, also by heating it with resorcinol.

3. The triacetate, monosodium salt, triammonium salt, monoammonium salt and dibromo derivatives of hydroxybenzoyltetrachloro-*o*-benzoic acid have been prepared.

4. The acetate and two ammonium compounds of this dibromo derivative have been prepared.

5. The dibromo derivative has been converted into tetrachloroeosin by heating the acid above its melting point.

6. A trichloro acid has been prepared by removal of one chlorine atom together with an atom of hydrogen from the tetrachloro acid. The resulting trichloro acid is a xanthone derivative.

7. The sodium and ammonium salts and the acetate of the trichloro acid have been prepared.

8. It seems highly probable from the results of this investigation that the formation of the phthaleins takes place in two steps: First, an addition product of the phenol and anhydride is formed analogous to the di-

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[1] THIS JOURNAL, **39**, 694 (1917).

hydroxy acid and this then reacts with a second molecule of the phenol with the loss of water to form the phthalein.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

HYDROCARBO BASES AND A STUDY OF ORGANIC DERIVATIVES OF MERCURY AND OF LEAD.

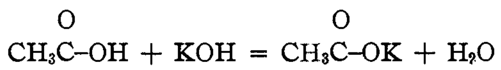
BY LAUDER W. JONES AND LOUIS WERNER.

Received May 14, 1918.

Introduction.

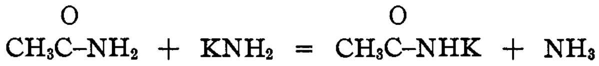
During the early development of the theory of Arrhenius, one of the most convincing arguments in support of his theory was the precise manner in which it explained the phenomenon of neutralization. The union of positive hydrogen ions with negative hydroxyl ions was fundamental to all processes of neutralization involving the interaction of aquo bases with aquo acids. Later, quantitative exactness was given to the explanation, when the ionization constant of water was determined in many independent ways, and the results were found to agree very closely, although the methods employed differed quite widely in character.

The interesting investigations of Franklin,[1] Kraus and others have familiarized us with a different class of bases and acids which have been called ammono bases and ammono acids. "The acids of this system are the acid amides and imides, including the amides and imides of non-metallic elements; the bases of the system are the metallic amides and imides, the salts are metal derivatives of acid amides and imides." As Franklin says, he "has developed a system of acids, bases and salts in which nitrogen occupies a position similar to that occupied by oxygen in the system of Lavoisier." The following equations illustrate the relations between aquo and ammono derivatives:



$$\mathrm{CH_3\overset{O}{C}{-}OH + KOH = CH_3\overset{O}{C}{-}OK + H_2O}$$

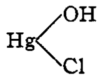
Aquo acid. Aquo base. Aquo salt.



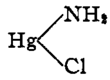
$$\mathrm{CH_3\overset{O}{C}{-}NH_2 + KNH_2 = CH_3\overset{O}{C}{-}NHK + NH_3}$$

Ammono acid. Ammono base. Ammono salt.

Basic salts of the ammono type exist:



Aquo basic salt.



Ammono basic salt.

Developments of this kind have inclined chemists[2] to favor a more com-

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[1] *Am. Chem. J.*, 45, 291 (1912).

[2] Stieglitz, "Qual. Chem. Anal.," 1, 177, note (1911).