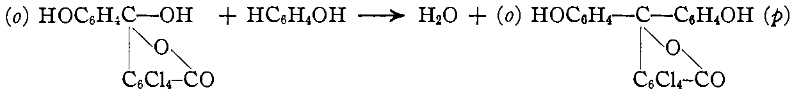
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

ORTHO-HYDROXYBENZOYL-ORTHO-TETRACHLOROBENZOIC ACID, ISOPHENOL-TETRACHLOROPHTHALEIN AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND THEOPHILUS PARSONS[1]

RECEIVED NOVEMBER 2, 1925 PUBLISHED JANUARY 8, 1926

Isophenolphthalein[2] has been made in this Laboratory by condensing *o*-hydroxybenzoyl-benzoic acid with phenol. Isophenol-tetrachlorophthalein was made in a similar manner by condensing *o*-hydroxybenzoyl-tetrachlorobenzoic acid with phenol using stannic chloride as the condensing agent



$$(o)\ \mathrm{HOC_6H_4}\underset{\mathrm{C_6Cl_4{-}CO}}{\underset{\diagdown\mathrm{O}\diagdown}{\mathrm{C}}}\mathrm{{-}OH} + \mathrm{HC_6H_4OH} \longrightarrow \mathrm{H_2O} + (o)\ \mathrm{HOC_6H_4{-}}\underset{\mathrm{C_6Cl_4{-}CO}}{\underset{\diagdown\mathrm{O}\diagdown}{\mathrm{C}}}\mathrm{{-}C_6H_4OH}\ (p)$$

o-Hydroxy acid Isophenol-tetrachlorophthalein

The *o*-hydroxy acid was made from tetrachlorophthalic acid anhydride and phenol by the method of Ullmann and Schmidt.[3]

A mixture of 57 g. of *pure* tetrachlorophthalic acid[4] and 250 cc. of acetylene tetrachloride was heated in a flask until all the water and some acetylene tetrachloride had distilled at the boiling point (147°) of the acetylene tetrachloride and the acid was completely converted into the anhydride. This was shown by the fact that the anhydride is soluble in acetylene tetrachloride, while the acid is not. Eighteen g. of phenol was added and the mixture heated at 110°. During the course of an hour 50 g. of pulverized aluminum chloride was added in small portions. After the addition of all of the aluminum chloride the heating was continued for three hours until the evolution of hydrogen chloride ceased. At the end the temperature of the bath was raised to 125° for five minutes. The mixture was poured into a large volume of dil. hydrochloric acid and distilled in steam to remove the aluminum chloride, acetylene tetrachloride and phenol. The *o*-hydroxy acid was filtered off and heated to boiling with a large volume of water several times to remove any unused tetrachlorophthalic acid. This crude *o*-hydroxy acid was then dissolved in dil. ammonia solution, giving a yellow solution with a slightly reddish tinge due to the presence of some phthalein. The solution was filtered, acidified with hydrochloric acid, and the yellow *o*-hydroxy acid filtered off and dried; m. p., 197°. It was recrystallized from xylene when it melted at 207° and was nearly colorless. It was further purified by recrystallization from glacial acetic acid when it was obtained colorless and melted at 210°. Analyses showed it to be pure.

Anal. Subs., 0.1444, 0.1551: AgCl, 0.2194, 0.2350. Calcd. for $C_{14}H_6O_4Cl_4$: Cl, 37.34. Found: 37.59, 37.48.

The yield of the crude acid was about 82%.

DIACETATE.—This was made by heating the acid with acetic anhydride and fused

---

[1] Work done in partial fulfilment of the requirements for the degree of Bachelor of Chemistry by Theophilus Parsons, holder of the Grasselli Undergraduate Scholarship in Chemistry at Cornell University, 1923–1924.

[2] Orndorff and Barrett, THIS JOURNAL, **46**, 2483 (1924)

[3] Ullmann and Schmidt, *Ber.*, **52**, 2098 (1919).

[4] See *Am. Chem. J.*, **41**, 414 (1909) and THIS JOURNAL, **40**, 1235 (1918).

sodium acetate. It was crystallized several times from ethanol and analyzed; m. p., 168°.

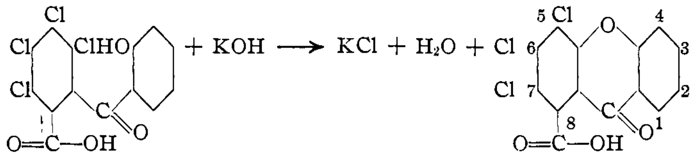
Anal. Subs., 0.1889, 0.1876: 16.37, 16.23 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{18}H_{10}O_6Cl_4$: Cl, 30.57. Found: 30.73, 30.68.

It is very easily soluble in benzene, easily soluble in glacial acetic acid and chloroform, soluble in ethanol and difficultly soluble in methanol. It dissolves in concd. sulfuric acid forming a bright orange solution that undergoes hydrolysis as the acid precipitates on the addition of water. The diacetate has a structure similar to that of the diacetate of *p*-hydroxybenzoyl-*o*-benzoic acid.[5] It is readily saponified by hot solutions of the alkalies, giving as the final product 5,6,7-trichloroxanthone-8-carboxylic acid.

5,6,7-Trichloroxanthone-8-carboxylic Acid.—Five g. of the *o*-hydroxy acid was heated with 50 cc. of 30% sodium hydroxide solution for one hour. The sodium salt which precipitated was decomposed with hydrochloric acid and the xanthone acid crystallized twice from 95% ethanol. On drying at 120° the crystals lost their crystalline form and some alcohol. The dried product was analyzed and proved to be pure 5,6,7-trichloroxanthone-8-carboxylic acid.

Anal. Subs., 0.3879, 0.2327: 33.75, 20.29 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{14}H_5O_4Cl_3$: Cl, 30.97. Found: 30.85, 30.92.

The xanthone acid melts at 262–265° with the evolution of a gas. It is easily soluble in chloroform, hot glacial acetic acid, and sparingly soluble in methanol and ethanol. Its solution in concd. sulfuric acid is greenish-yellow. The formation of the xanthone acid proves that the hydroxyl group is in the ortho position in hydroxybenzoyl-tetrachlorobenzoic acid. The reaction is as follows.



o-Hydroxy acid

5,6,7-Trichloroxanthone-8-carboxylic acid

In order to show that this compound contains a carboxyl group the barium and sodium salts were made.

Barium Salt.—This was made by boiling the xanthone acid suspended in alcohol with a slight excess of barium hydroxide solution, and filtering off the insoluble barium salt. It was dried at 120° and analyzed.

Anal. Subs., 0.1545: $BaSO_4$, 0.0434. Calcd. for $(C_{14}H_4O_4Cl_3)_2Ba$: Ba, 16.71. Found: 16.53.

Subs., 0.1601, 0.1230: 11.64, 8.92 cc. of 0.1 *N* $AgNO_3$. Calcd.: Cl, 25.87. Found: 25.78, 25.71.

The salt is sparingly soluble in water and insoluble in ethanol.

Sodium Salt.—This was made in the same way as the barium salt. The precipitate which consisted of minute colorless crystals was dried at 120° and analyzed.

Anal. Subs., 0.1319: Na_2SO_4, 0.0255. Calcd. for $C_{14}H_4O_4Cl_3Na$: Na, 6.29. Found: 6.26.

Subs., 0.2595, 0.2646: 21.22, 21.67 cc. of 0.1 *N* $AgNO_3$. Calcd.: Cl, 29.11. Found: 29.00, 29.04.

---

[5] Orndorff and Kelley, This Journal, **44**, 1522 (1922).

The sodium salt is only slightly soluble in 95% ethanol and sparingly soluble in water. It is precipitated when a solution of an alkali is added to its aqueous solution.

Preparation of Isophenol-tetrachlorophthalein.—A mixture of 30 g. of *o*-hydroxybenzoyl-*o*-tetrachlorobenzoic acid, dissolved in 15 g. of redistilled phenol, with 20 g. of stannic chloride was heated in the oil-bath at 95–100° for 24 hours. The mass was treated with dil. hydrochloric acid and distilled in steam to remove phenol. The phthalein was filtered from the stannic chloride solution, dried and weighed; yield, 27 g., or 74%. The tetrachlorofluoran amounting to 2 g. was separated from the phthalein by dissolving the latter in 2% sodium hydroxide solution, filtering, and precipitating with hydrochloric acid. The isophenol-tetrachlorophthalein was crystallized twice from methanol; m. p., 293°. The substance was dried at 85° and analyzed.

Anal. Subs., 0.2127, 0.1995: 18.51, 17.38 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{20}H_{10}O_4Cl_4$: Cl, 31.11. Found: 30.86, 30.89.

Isophenol-tetrachlorophthalein is soluble in methanol, ethanol and benzene, less soluble in glacial acetic acid, toluene and chloroform. It dissolves in concd. sulfuric acid giving a deep red solution, the color of which fades to a pale lemon-yellow on standing. It dissolves in solutions of the alkalies and ammonia and the resulting solutions are purple. In a concentrated solution of ammonia it gives a blue color. The Sörensen value (*P*H) at the end-point (reddish-violet color) was found to be 9.2. The melting point of phenol-tetrachlorophthalein, which is not given in the literature, is 307°.

Tetrachlorofluoran.—This substance is a by-product of the preparation of isophenol-tetrachlorophthalein from which it is separated by reason of its insolubility in solutions of the alkalies.

It was purified by dissolving in benzene, boiling the solution with bone black until colorless, concentrating the solution and allowing it to cool. After further recrystallization from benzene the colorless substance was analyzed.

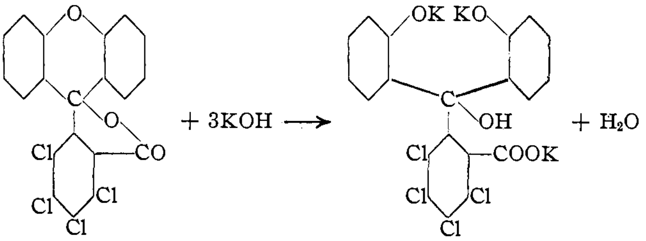
Anal. Subs., 0.2038, 0.1600: 18.51, 14.60 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{20}H_8O_3Cl_4$: Cl, 32.38. Found: 32.20, 32.36.

Tetrachlorofluoran melts with decomposition at 298°. Orndorff and Black[6] obtained tetrachlorofluoran as a by-product of the preparation of phenol-tetrachlorophthalein from tetrachlorophthalic acid and phenol. They state that it does not melt when heated to 300°. This is evidently an error. We have determined the melting point of tetrachlorofluoran obtained as a by-product in the preparation of phenol-tetrachlorophthalein from tetrachlorophthalic acid and phenol and also of the tetrachlorofluoran obtained as a by-product in the preparation of isophenol-tetrachlorophthalein, and both products as well as a mixture of the two melt at 298° with decomposition.

Orndorff and Black[6] found that when tetrachlorofluoran was heated in an alcoholic solution of potassium hydroxide for eight hours at the boiling point with ethyl iodide, they obtained a product which contained only 21.72% of chlorine and they state that "chlorine has been removed and the

[6] Orndorff and Black, *Am. Chem. J.*, **41**, 349 (1909).

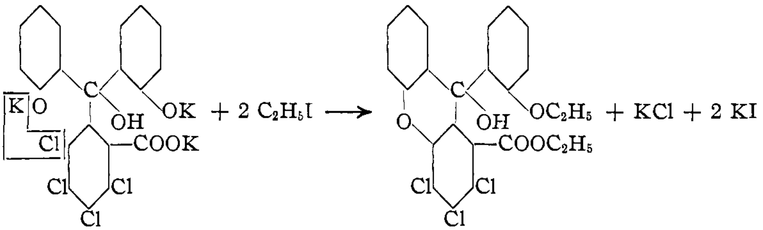
product is not a derivative of tetrachlorofluoran." It is quite possible that the action of the alcoholic potassium hydroxide solution at the boiling point on the tetrachlorofluoran gives the tripotassium salt of the carbinol carboxylic acid,



Tetrachlorofluoran

Tripotassium salt of the carbinol carboxylic acid

and that this reacts with ethyl iodide, splitting off potassium chloride and potassium iodide:



giving an ether ester of a *trichloro* acid. A compound of this formula would have 21.55% of chlorine and this agrees very well with the amount found, 21.72%. The fact that chlorine splits off with potassium is in accord with the fact that the hydroxyl group is in the *ortho* position to the methane carbon atom in the tripotassium salt of the carbinol carboxylic acid, as shown in the above formula.

Derivatives of Isophenol-tetrachlorophthalein

Diacetate.—This was made by boiling the isophthalein with acetic anhydride. It was dissolved in benzene, the benzene removed by distillation and the thick sirup dissolved in 95% ethanol. From this solution colorless needles separated; m. p., 189°. The product dried at 170° was analyzed.

Anal.[7] Subs., 0.1546, 0.1849: AgCl, 0.1652, 0.1945. Calcd. for $C_{20}H_8O_2Cl_4(OCOCH_3)_2$: Cl, 26.27. Found: 26.43, 26.02.

The diacetate is very soluble in benzene, glacial acetic acid and hot chloroform, soluble in ethanol and very difficultly soluble in methanol. The structure of the diacetate is similar to that of the diacetate[6] of phenol-tetrachlorophthalein, which melts at 205–206°.

Dibenzoate.—Twenty-five cc. of benzoyl chloride and 5 g. of isophenol-tetrachlorophthalein were heated together on the water-bath for six hours. The excess of benzoyl chloride was then removed by heating the mixture in a water-oven through which passed

---

[7] These analyses were made by Dr. R. T. K. Cornwell.

a current of dry air. The residue was crystallized from boiling xylene. The colorless crystals were recrystallized from acetone; m. p., 245°.

Anal. Subs., 0.4337, 0.2309: wt. after drying at 180°, 0.4306, 0.2292; AgCl, 0.3640, 0.1950; loss, 0.74%. Calcd. for $C_{34}H_{18}O_6Cl_4$: Cl, 21.36. Found: (dried sample) 20.91, 21.05.

The dibenzoate is very soluble in benzene, easily soluble in acetone, chloroform, and boiling xylene, soluble in ethanol, sparingly soluble in glacial acetic acid, and difficultly soluble in methanol. Its solution in concd. sulfuric acid is red and undergoes saponification. It is also saponified slowly on heating with dilute solutions of the alkalies. Its structure is similar to that of the diacetate of phenol-tetrachlorophthalein.[6]

Dimethyl Ether.—Five g. of isophenol-tetrachlorophthalein was dissolved in a solution of 10 g. of sodium hydroxide in 100 cc. of water; 2 g. of dimethyl sulfate was added in small portions during constant shaking. After standing overnight the yellow amorphous precipitate was filtered off and boiled with dil. sodium hydroxide solution to remove any unchanged phthalein monomethyl ether, and to saponify any methyl ester that might have been formed. The dimethyl ether was then filtered off, washed with water, dried in the air, and crystallized from 95% ethanol, after decolorization of the solution with bone black. After recrystallization from 95% ethanol the colorless crystals were dried at 120° and analyzed.

Anal. Subs., 0.1947, 0.1828: 16.03, 15.08 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{20}H_8O_2Cl_4(OCH_3)_2$: Cl, 29.30. Found: Cl, 29.19, 29.25.

The dimethyl ether melts at 183°. It is very easily soluble in benzene, soluble in methanol and sparingly soluble in ethanol. It is insoluble in alkaline solutions. Its solution in concd. sulfuric acid is a deep blood-red and the substance is precipitated unchanged from this solution upon addition of water. Its structure is similar to that of the dimethyl ether of phenol-tetrachlorophthalein,[6] which melts at 152–153°.

Summary

1. *o*-Hydroxybenzoyl-*o*-tetrachlorobenzoic acid has been prepared by condensing the anhydride of tetrachlorophthalic acid with phenol in solution in acetylene tetrachloride using aluminum chloride as the condensing agent. As it is colorless and yields a colorless diacetate it probably has the lactone structure. The salts are yellow and have the ketone structure.

2. 5,6,7-Trichloroxanthone-8-carboxylic acid is formed by the action of solutions of the alkalies on *o*-hydroxybenzoyl-*o*-tetrachlorobenzoic acid, thus proving the structure of the latter acid. Barium and sodium salts of 5,6,7-trichloroxanthone-8-carboxylic acid have been prepared, thus showing the presence of the carboxyl group.

3. *o*-Hydroxybenzoyl-*o*-tetrachlorobenzoic acid condenses with phenol to form isophenol-tetrachlorophthalein and a small amount of tetrachlorofluoran when stannic chloride is used as the condensing agent.

4. As isophenol-tetrachlorophthalein is colorless and forms a colorless diacetate, dibenzoate and dimethyl ether, it has the lactone structure and contains two hydroxyl groups. It dissolves in solutions of the alkalies forming deep purple liquids, and these solutions probably contain orthoquinoid salts.[2]

5. From the method of preparation of isophenol-tetrachlorophthalein one hydroxyl group must be in the *ortho* position and the other in the *para* position to the methane carbon atom; that is, it is the tetrachloro derivative of isophenolphthalein in which the four chlorine atoms are in the phthalic acid residue.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE, AND THE CHEMICAL INSTITUTE OF THE UNIVERSITY OF BERLIN]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP.[1] XI[2] THE RELATED ROTATIONS OF AMYLOBIOSE, AMYLOTRIOSE AND GLUCOSE

BY C. S. HUDSON, H. PRINGSHEIM AND J. LEIBOWITZ

RECEIVED NOVEMBER 21, 1925 PUBLISHED JANUARY 8, 1926

It has been shown[3] that the rotations of many of the compound sugars can be mathematically expressed in terms of the rotations of the constituent sugars by formulas derived from the application of the Van't Hoff hypothesis of optical superposition. Doubtless, this method of correlating rotation with structure can eventually be applied to all compound sugars and polysaccharides since the extent of the applications that have so far been made of it have been limited only by the extent of our knowledge of the structures of compound sugars. It was successfully applied to the group of compound sugars that possess in common the "sucrose union" (namely, sucrose, raffinose, gentianose and stachyose), and from it conclusions were drawn concerning structural features of trehalose, lactose, cellobiose[3] and amygdalin.[4] It is the purpose of the present article to indicate the application of this method to the problem of the structures of amylobiose and amylotriose, the two sugars which have recently been shown to be the units from which the starch molecule is constructed.[5] It will be shown that if the structural formulas proposed by Pringsheim for these sugars are correct, and the Van't Hoff hypothesis holds for these substances, a certain simple numerical relationship should apply among the rotations of glucose, amylobiose and amylotriose. An experimental test verifies this theoretical deduction both for the case of the sugars themselves and for that of their acetates. The numerical relationship that is thus established may be regarded as a fact, independent of theory, with which any structural formulas that may be proposed for

---

[1] Published by permission of the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] Part X was published in THIS JOURNAL, **47,** 2052 (1925).

[3] Hudson, *ibid.*, **38,** 1566 (1916).

[4] Hudson, *ibid.*, **46,** 483 (1924).

[5] Pringsheim, *Ber.*, **57,** 1581 (1924).