

105–110°. It is a tautomeric substance, and colored derivatives of the quinoid form (salts) and colorless derivatives of the lactoid form (diacetate, dibenzoate and dimethyl ether) have been made.

2. The colorless dimethyl ether of *m*-cresolsulfonephthalein is converted into a colored quinoid form at 170–172°.

3. Tetrabromo-*m*-cresolsulfonephthalein and its diacetate and dibenzoate have been made. All three are colorless and, therefore have the lactoid structure. Tetrabromo-*m*-cresolsulfonephthalein forms a colored quinoid hydrate and an ammonium salt.

4. Pure 3,6-dimethylsulfonefluoran was prepared by the condensation of *m*-cresol with the anhydride of *o*-sulfobenzoic acid at 125–145°. Unlike the fluorans previously investigated, it is a colored compound and is slightly soluble in water. It is a weak acid and does not form stable salts nor does it absorb dry ammonia gas. With dry hydrogen chloride it gives a colored hydrochloride, analogous to that obtained with 3,6-dimethylfluoran.

5. The colorless zinc salt of the reduction product of 3,6-dimethylsulfonefluoran (3,6-dimethylhydrosulfofluoranic acid) was made.

6. Pure dibromo-3,6-dimethylsulfonefluoran was prepared. It is a colored compound and therefore has the quinoid structure. It absorbs dry ammonia gas and yields a stable ammonia compound due to the introduction of the two bromine atoms.

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

### 3-HYDROXY-TETRACHLOROFLUORAN AND 3,4-DIHYDROXY-TETRACHLOROFLUORAN AND SOME OF THEIR DERIVATIVES

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RECEIVED MAY 29, 1926

PUBLISHED AUGUST 5, 1926

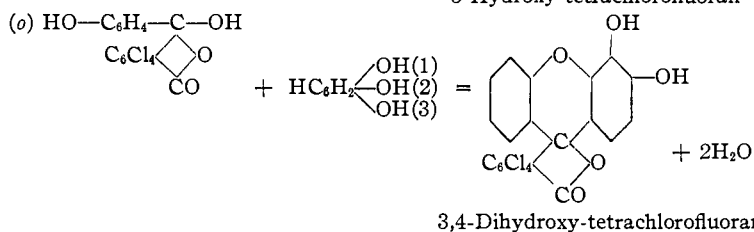
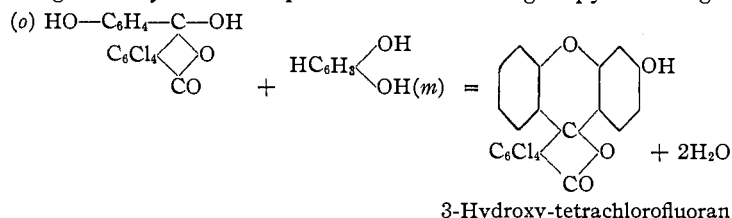
It has been shown in this Laboratory that the formation of the phthaleins from phthalic anhydride and the phenols proceeds in two stages; first, the phenol combines with the anhydride to form the intermediate acid, *p*-hydroxybenzoyl-*o*-benzoic acid in the case of phenol itself, then this acid reacts with another molecule of the phenol to give the phthalein and water. Isophenolphthalein was prepared by Orndorff and Barrett<sup>2</sup> by condensing *o*-hydroxybenzoyl-*o*-benzoic acid with phenol, and Orndorff and Parsons<sup>3</sup> have made isophenol-tetrachlorophthalein from *o*-hydroxybenzoyl-tetra-

<sup>1</sup> From a dissertation presented to the Faculty of the Graduate School of Cornell University, by C. H. Johnson, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Orndorff and Barrett, *THIS JOURNAL*, **46**, 2483 (1924).

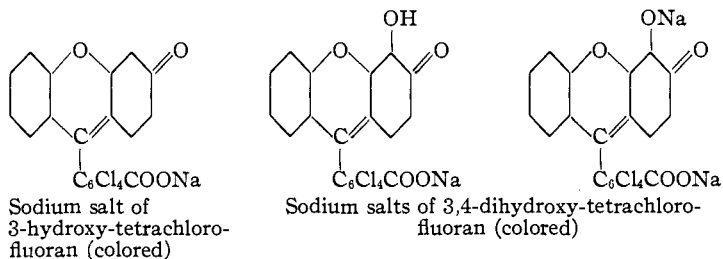
<sup>3</sup> Orndorff and Parsons, *ibid.*, **48**, 283 (1926).

chloro-*o*-benzoic acid and phenol. It was thought that *o*-hydroxybenzoyl-tetrachloro-*o*-benzoic acid would condense with resorcinol and with pyrogallol to give *unsymmetrical* phthaleins containing a pyrone ring.



As these *unsymmetrical* phthaleins had never been made and it was desirable to investigate them and study their absorption spectra, the present investigation was undertaken.

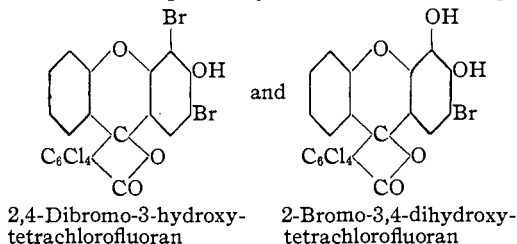
Both of these compounds have now been made by the method described above, and as they are *colorless* they both have the *lactoid* formulas given above. Their salts are colored, however, and have *quinoid* structures.



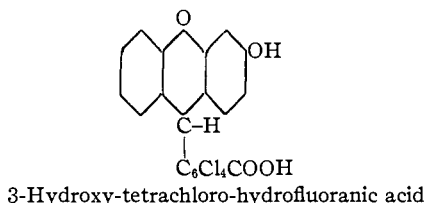
The 3-hydroxy-tetrachlorofluoran gives a mono-acetate and a mono-benzoate both of which are colorless and have the *lactoid* structure. The formation of these substances shows the presence of one hydroxyl group in the *lactoid* form of the phthalein. The 3,4-dihydroxy-tetrachlorofluoran gives a *colorless* diacetate and dibenzoate as well as a *colorless* monobenzoate, all of which have the *lactoid* structure. The formation of the diacetate and the dibenzoate shows the presence of two hydroxyl groups in the *lactoid* form of the phthalein. It will thus be seen that the *unsymmetrical* phthaleins, like the symmetrical, act as tautomeric substances.

2,4-Dibromo-3-hydroxy-tetrachlorofluoran is colorless, and has the *lactoid* structure. It yields a colorless mono-acetate, but forms colored

salts. 3,4-Dihydroxy-tetrachlorofluoran gives a monobromo derivative which is colorless and forms a colorless diacetate, but its salts are colored. These bromine derivatives of the unsymmetrical phthaleins also act as tautomeric substances and probably have the following structures.



Like the symmetrical phthaleins, these *unsymmetrical* compounds readily undergo reduction to compounds corresponding to the *phthalins*. 3-Hydroxy-tetrachloro-hydrofluoran, formed by the reduction of the corresponding fluoran, is analogous to hydrofluoran, and has the following structure as it is colorless and dissolves in alkalis without color.



It yields a colorless mono-acetate which is soluble in alkalis. It is interesting to note that neither of these *unsymmetrical* phthaleins exhibits fluorescence in alkaline solution.

### Experimental Part

**Preparation of *o*-Hydroxy-benzoyltetrachloro-*o*-benzoic Acid.**—This acid was prepared following the directions of Orndorff and Parsons.<sup>3</sup> Analyses and melting-point determinations proved it to be very nearly pure, and it was, therefore, used directly in the work that follows.

### 3-Hydroxy-tetrachlorofluoran

**Preparation.**—This compound was prepared from resorcinol and the *o*-hydroxy acid mentioned above. Attempts to prepare it by heating them together, both with and without a condensing agent, at temperatures ranging from 130° to 220° were not successful, since the main product was tetrachloro-fluorescein.<sup>4</sup> Moreover it was very difficult to extract the last traces of tetrachloro-fluorescein from the hydroxy-tetrachlorofluoran, although the former is much more soluble in dilute aqueous alkalis than

<sup>4</sup> Orndorff and Hitch, *THIS JOURNAL*, **36**, 680 (1914).

the latter. The formation of tetrachloro-fluorescein is due to the thermal decomposition of the *o*-hydroxy acid and also to condensation of resorcinol with the tetrachloro-phthalic anhydride thus liberated. At the higher temperatures a sublimate of this anhydride on the cooler portions of the flask and air condenser gave additional evidence of the decomposition of the *o*-hydroxy acid by heat.

A method was finally worked out which insured a homogeneous mixture of the reacting substances with the condensing agent at comparatively low temperatures. No tetrachloro-fluorescein is formed by this method, provided the temperature is kept below 130°.

Fifty g. of the *o*-hydroxybenzoyl-tetrachloro-*o*-benzoic acid and 30 g. of resorcinol were ground together and the mixture was added to 150 cc. of acetylene tetrachloride. To this was added 35 g. of fuming stannic chloride. A reddish color developed immediately. The mixture was heated at 120° to 125° for about 24 hours, and the flask shaken frequently during the first hour to dissolve the reagents. As the reaction proceeded, the color of the solution deepened to a very dark red, and the hydroxy-tetrachloro-fluoran settled to the bottom in the form of a reddish-brown tar. At the end of the heating period both the liquid and the tar were transferred to a flask with the aid of steam or hot water. The solvent and the excess of resorcinol were removed by steam distillation, leaving the hydroxy-tetrachlorofluoran as a partially crystalline, orange-yellow solid. This was dried, first at room temperature and then at 120°. The finely divided, orange-yellow powder weighed 60 g. It was completely soluble in a large volume of 1% sodium hydroxide solution. This was poured slowly into an excess of dil. hydrochloric acid, during mechanical stirring. This treatment gave a flocculent, orange-yellow precipitate which was finally dried at 120° and extracted several times with boiling benzene. The combined extracts were boiled with bone black, filtered and about two-thirds of the solvent distilled. From the yellow solution a crop of colorless crystals separated after several hours. Those isolated had a definite crystal form, being short thick needles similar to the crystals of tetrachlorofluoran itself. Subsequent distillations of the solvent gave more colorless crystals until the volume became quite small and impurities gave the solution a red color. The yield was 45 g., or about 75% of that calculated. In later work the alkali treatment was omitted, since the colorless crystals are as readily obtained by extracting the crude product with benzene. A portion of the colorless crystals was recrystallized from benzene, dried to constant weight at 150° and analyzed.

*Anal.* Subs., 0.1539, 0.1514: cc. of 0.1 *N* AgNO<sub>3</sub>, 13.5, 13.3. Calcd. for C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>4</sub>: Cl, 31.25. Found: 31.11, 31.15.

**Properties.**—The colorless, crystalline product dissolves in dilute aqueous alkalis with development of an orange-red color. It shows no visible fluorescence. It dissolves in concd. sulfuric acid also forming an orange-red solution, and is precipitated therefrom by water. It is slightly soluble in carbon disulfide, ether and petroleum ether, and in glacial acetic acid; soluble in ethanol and methanol with development of a yellow color if a trace of water is present; in chloroform, ethyl acetate and acetone; and in benzene, which is the best solvent for it. The compound is colorless in dilute acid solution, and remains so up to and including *P<sub>H</sub>* 5.6. It is distinctly yellow at *P<sub>H</sub>* 6.0. The compound does not melt when heated to 300°. It has the lactoid structure in the solid form and in the acetate and benzoate, but forms colored salts having the quinoid form.

**MONO-ACETATE.**—Five g. of the hydroxy-tetrachlorofluoran was boiled with 30 cc. of acetic anhydride and 3 g. of fused sodium acetate. The crude, yellow product was

purified by crystallization from aqueous acetone, after being decolorized with bone black. The colorless flakes thus secured melted at 198–200°. The acetate is slowly hydrolyzed by dilute aqueous alkalis and by concd. sulfuric acid, giving to the solutions the same orange-red color as the hydroxy-tetrachlorofluoran. It is soluble in acetone, benzene, ethanol and methanol, and in ether. The flakes from acetone were prepared for analysis by drying to constant weight at 150°.

*Anal.* Subs., 0.1547, 0.1713: cc. of 0.1 *N* AgNO<sub>3</sub>, 12.5, 13.75. Calcd. for C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>(COCH<sub>3</sub>): Cl, 28.6. Found: 28.65, 28.46.

**MONOBENZOATE.**—Five g. of the hydroxy-tetrachlorofluoran was boiled with 50 cc. of benzoyl chloride. When the cooled solution was poured into an equal volume of absolute alcohol a colorless, granular substance settled out which, after being washed with alcohol and dried at room temperature, melted at 248–249°. Like the acetate it is hydrolyzed by alkalis and by concd. sulfuric acid, but more slowly. It is soluble in benzene, acetone, ether and ethanol. The air-dried material was heated to constant weight at 160°.

*Anal.* Subs., 0.1752, 0.1536: cc. of 0.1 *N* AgNO<sub>3</sub>, 12.5, 11.0. Calcd. for C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>(COC<sub>6</sub>H<sub>5</sub>): Cl, 25.42. Found: 25.30, 25.39.

**MONO-AMMONIUM SALT.**—In an attempt to make the imide<sup>2</sup> by the action of concd. ammonia solution on the hydroxy-tetrachlorofluoran, the ammonium salt, in the form by glistening, red-brown flakes, was obtained. After recrystallization from ethanol and drying, it melted at 277–280° with decomposition. It is soluble in ethanol, methanol, benzene and acetone.

*Anal.* Subs., 0.1588, 0.1548: cc. of 0.1 *N* AgNO<sub>3</sub>, 13.6, 13.2. Calcd. for C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>NH<sub>4</sub>: Cl, 30.12. Found: 30.37, 30.24.

**MONOSODIUM SALT.**—Five g. of the 3-hydroxy-tetrachlorofluoran was suspended in about half a liter of ethanol and an excess of freshly prepared sodium ethylate solution added. After boiling for about three hours, half the solvent had distilled and the orange-red salt gradually crystallized. After recrystallization from ethanol, the air-dried substance did not melt when heated to 300°. It lost little weight when heated at 140°.

*Anal.* Subs., 0.1803, 0.1931: cc. of 0.1 *N* AgNO<sub>3</sub>, 15.3; Na<sub>2</sub>SO<sub>4</sub>, 0.0287. Calcd. for C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>Na: Cl, 29.80; Na, 4.83. Found: Cl, 30.09; Na, 4.81.

**BARIUM SALT.**—Three g. of the crude sodium salt was dissolved in a large volume of very dilute ammonia solution. To the filtered solution was added a slight excess of dil. barium chloride solution. The crude barium salt which precipitated immediately was dried and recrystallized from a mixture of benzene and methanol. The well-formed, orange-red crystals contain about three molecules of water. They are slightly soluble in water and soluble in ethanol, methanol and benzene. The dry substance decomposes when heated slightly above 300°.

*Anal.* Subs., 0.2364: loss at 165°, 0.0211. Calcd. for (C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>)<sub>2</sub>Ba + 3H<sub>2</sub>O: H<sub>2</sub>O, 9.39. Found: 8.76.

Subs. (dry), 0.1888, 0.1667: BaSO<sub>4</sub>, 0.0418, 0.0376. Calcd. for (C<sub>20</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>)<sub>2</sub>Ba: Ba, 13.17. Found: 13.03, 13.27.

**2,4-Dibromo-3-hydroxy-tetrachlorofluoran.**—Ten g. of the hydroxy-tetrachlorofluoran was suspended in 150 cc. of glacial acetic acid, and a slight excess of bromine over that calculated for the formation of a tetrabromo derivative was dissolved in a little of the same solvent and added slowly during stirring. After standing for 12 hours and heating on the steam-bath for two hours there was still considerable bromine left. The cream-colored precipitate was filtered off and washed with 80% acetic acid and with water. The color was removed by recrystallization from benzene. The pure substance

does not melt when heated to 300°, nor does it lose appreciable weight when heated at 160°.

*Anal.* Subs., 0.1041, 0.1235: AgCl + AgBr, 0.1597, 0.1892: cc. of 0.1 *N* AgNO<sub>3</sub>, 10.1, 11.95. Calcd. for C<sub>20</sub>H<sub>5</sub>O<sub>4</sub>Cl<sub>4</sub>Br<sub>2</sub>: Cl, 23.18; Br, 26.12. Found: Cl, 22.98, 22.70; Br, 25.73, 26.02.

The dibromo derivative dissolves in concd. sulfuric acid with development of an orange color. It is less soluble in dilute alkalis than the hydroxy-tetrachlorofluoran, and no sodium salt is formed when it is boiled with a slight excess of sodium ethylate solution. The compound dissolves readily in benzene and acetone; it is less soluble in ethanol and glacial acetic acid, and insoluble in water.

**MONO-ACETATE.**—Three g. of the dibromo-hydroxy-tetrachlorofluoran was boiled with 1 g. of fused sodium acetate and 20 cc. of acetic anhydride. To remove the color the dried compound was dissolved in benzene and boiled with a little bone black. Crystals were secured by boiling off most of the benzene and adding methanol. They retained slightly more than a molecule of benzene, and melted at 290–292°, giving a red liquid.

*Anal.* Subs., 0.8528: loss at 140°, 0.0997. Calcd. for C<sub>20</sub>H<sub>5</sub>O<sub>4</sub>Cl<sub>4</sub>Br<sub>2</sub>(COCH<sub>3</sub>) + C<sub>6</sub>H<sub>6</sub>: C<sub>8</sub>H<sub>8</sub>, 10.67. Found: 11.69.

Subs. (heated to 140°), 0.1533, 0.1220; AgCl + AgBr, 0.2208, 0.1757: cc. of 0.1 *N* AgNO<sub>3</sub>, 14.0, 11.2. Calcd. for C<sub>20</sub>H<sub>5</sub>O<sub>4</sub>Cl<sub>4</sub>Br<sub>2</sub>(COCH<sub>3</sub>): Cl, 21.70; Br, 24.45. Found: Cl, 22.06, 22.10; Br, 23.50, 23.23.

The mono-acetate is slowly hydrolyzed by dilute alkalis and quickly by concd. sulfuric acid. It is very soluble in acetone and in benzene, and dissolves in glacial acetic acid, ether and ethanol.

**Reduction of 3-Hydroxy-tetrachlorofluoran.**—Five g. of the hydroxy-tetrachlorofluoran and an equal weight of zinc dust were suspended in about half a liter of glacial acetic acid and the mixture was boiled for five hours. At the end of this time a test portion, made alkaline with sodium hydroxide, failed to give a red color, which indicated that reduction was complete. The reduction product was precipitated with boiled water, working as much as possible in an atmosphere of carbon dioxide. The dried material was crystallized from benzene; m. p., 257–258°. It is soluble in dilute alkalis with development of only a slight yellow color but soon oxidizes to the original hydroxy-tetrachlorofluoran which then gives the red color. The reduction product is much more soluble in ether than the hydroxy-tetrachlorofluoran, and dissolves readily in acetone, benzene and ethanol. The crystals from benzene were prepared for analysis by heating in a current of carbon dioxide at 140°.

*Anal.* Subs., 0.1462, 0.1398: cc. of 0.1 *N* AgNO<sub>3</sub>, 12.8, 12.2. Calcd. for C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>Cl<sub>4</sub>: Cl, 31.11. Found: 31.04, 30.94.

The reduction product described above is a derivative of hydrofluoric acid.<sup>5</sup> It is therefore called 3-hydroxy-tetrachloro-hydrofluoric acid.

**Mono-acetate of 3-Hydroxy-tetrachloro-hydrofluoric Acid.**—Three g. of the freshly prepared acid was converted into the acetate by boiling with sodium acetate and acetic anhydride. It was purified by crystallization from benzene; m. p. (dry), 187–188°.

*Anal.* Subs., 0.1602, 0.1709: cc. of 0.1 *N* AgNO<sub>3</sub>, 12.8, 13.7. Calcd. for C<sub>20</sub>H<sub>9</sub>O<sub>4</sub>Cl<sub>4</sub>(COCH<sub>3</sub>): Cl, 28.48. Found: 28.33, 28.42.

The mono-acetate is soluble in benzene, acetone, ethanol and ether. It dissolves very slowly in aqueous alkalis with a pale yellow color which changes to orange-red on long standing, due to oxidation.

<sup>5</sup> Meyer and Hoffmeyer, *Ber.*, **25**, 2118 (1892).

### 3,4-Dihydroxy-tetrachlorofluoran

**Preparation.**—This compound was prepared by the method used for the monohydroxy-tetrachlorofluoran, substituting 35 g. of pyrogallol for the resorcinol and increasing the solvent to about 200 cc. During the condensation the color of the mixture became successively red, violet-red and finally a dark brown. The dihydroxy-tetrachlorofluoran separated in the form of a black tar. It was worked up in the same manner as the monohydroxy compound and weighed 92 g. The crude material was extracted with about 5 liters of boiling benzene, from which it was obtained in the form of reddish-brown or gray-green, thick needles, the color depending on the concentration of the solution. It seems probable that the pure compound is colorless since the colors and shades vary with successive crystallizations, and since it was possible to obtain crystals possessing only a very pale tint of the above colors. Samples were heated to constant weight at 160°.

*Anal.* Subs., 0.1551, 0.1525, 0.1818: cc. of 0.1 N AgNO<sub>3</sub>, 13.1, 12.9, 15.3. Calcd. for C<sub>20</sub>H<sub>8</sub>O<sub>8</sub>Cl<sub>4</sub>: Cl, 30.19. Found: 29.95, 29.98, 29.84.

The benzene-soluble material amounted to 41 g.; yield, about 65%. There remained of the crude material about 52 g. of grayish-black powder only slightly soluble in this solvent. Efforts to crystallize it from various solvents failed. It gives a dirty brown precipitate with dilute alkalis, and probably is partially oxidized pyrogallol together with stannic acid. If the condensation is carried out at lower temperatures, and especially if for shorter times (up to 12 hours) this material is obtained in large quantity.

**Properties.**—This compound dissolves in dilute aqueous alkalis with development of a very deep blue color, and is precipitated therefrom as a flocculent brown precipitate on the addition of dilute acids. It dissolves in concd. sulfuric acid forming a deep red solution and is reprecipitated by water. It has about the same solubilities as the monohydroxy-tetrachlorofluoran, and gives a *pink* color to ethanol and to methanol if these solvents contain a little moisture. In dilute acid solutions the compound is colorless and remains so up to and including *P<sub>H</sub>* 4.8. From *P<sub>H</sub>* 5.2 to 8.8 inclusive the color is pink. At *P<sub>H</sub>* 9.2 it becomes distinctly blue. It does not melt when heated to 300°. 3,4-Dihydroxy-tetrachlorofluoran is isomeric with tetrachloro-fluorescein, but it shows no visible fluorescence in alkaline solution. It resembles tetrachlorogallein more closely in its behavior. The blue alkaline solution very slowly becomes pink and then pale yellow due to oxidation.

**DIACETATE.**—Seven g. of the dihydroxy-tetrachlorofluoran was boiled with 40 cc. of acetic anhydride and 4 g. of fused sodium acetate. The crude yellow-gray substance was dried and purified by repeated crystallization from aqueous acetone, after it had been decolorized with bone black. The small flakes thus secured retain a slight grayish tint; m. p., 215–220°, with some decomposition. The diacetate is slowly hydrolyzed by dilute alkalis and by concd. sulfuric acid. It is soluble in acetone, benzene, ether, and in ethanol and methanol. The flakes from acetone lost no appreciable weight when heated at 150°.

*Anal.* Subs., 0.1660, 0.1817: cc. of 0.1 N AgNO<sub>3</sub>, 11.9, 13.0. Calcd. for C<sub>20</sub>H<sub>6</sub>O<sub>8</sub>Cl<sub>4</sub>(COCH<sub>3</sub>)<sub>2</sub>: Cl, 25.61. Found: 25.42, 25.37.

**DIBENZOATE.**—Five g. of the dihydroxy-tetrachlorofluoran was boiled with 50 cc. of benzoyl chloride. The excess of benzoyl chloride was removed by heating the flask on a steam-bath while passing a current of air into it. The dark brown solid resulting from this treatment was dissolved in benzene and decolorized with bone black. It was obtained in crystalline form by adding ethanol and distilling part of the mixed solvent. The colorless crystals were well formed and contained one-half a molecule of benzene

after being air dried at room temperature; m. p.,  $140^{\circ}$ , again at  $220^{\circ}$ . Like the acetate it is hydrolyzed by alkalis and by concd. sulfuric acid, but more slowly. It dissolves very readily in the usual organic solvents, even at room temperature.

*Anal.* Subs., 0.1894, 0.1933: loss at  $150^{\circ}$ , 0.0098, 0.0102. Calcd. for  $C_{20}H_6O_5Cl_4(COC_6H_5)_2 + 0.5C_6H_6$ :  $C_6H_6$ , 5.44. Found: 5.17, 5.28.

Subs. (heated to  $150^{\circ}$ ), 0.1796, 0.1831: cc. of 0.1 *N*  $AgNO_3$ , 10.5, 10.8. Calcd. for  $C_{20}H_6O_5Cl_4(COC_6H_5)_2$ : Cl, 20.93. Found: 20.73, 20.92.

**MONOBENZOATE.**—Three g. of the dihydroxy-tetrachlorofluoran was dissolved in about 35 cc. of 1% sodium hydroxide solution and 3.5 cc. of benzoyl chloride was added slowly during vigorous shaking. After half an hour the gray-brown precipitate was filtered off and washed with a large volume of water. The dried material was extracted with benzene, and after it had been decolorized with bone black, colorless crystals were obtained by distilling part of the solvent and allowing the solution to cool; m. p. (air-dried),  $238-240^{\circ}$ . They are somewhat more readily hydrolyzed than the dibenzoate and are readily soluble in the usual organic solvents. A portion was dried to constant weight at  $160^{\circ}$ .

*Anal.* Subs., 0.1435, 0.1702: cc. of 0.1 *N*  $AgNO_3$ , 9.9, 11.8. Calcd. for  $C_{20}H_7O_5Cl_4(COC_6H_5)$ : Cl, 24.72. Found: 24.46, 24.59.

It is of interest to note that tetrachloro-fluorescein<sup>4</sup> forms a monobenzoate by the Baumann-Schotten reaction and a dibenzoate when boiled with benzoyl chloride.

**MONOSODIUM SALT.**—Five g. of the dihydroxy-tetrachlorofluoran was suspended in a liter of 95% ethanol and boiled with 2.5 g. of sodium acetate for about five hours. The crude product was obtained by distilling part of the solvent and cooling the solution. It was recrystallized from ethanol, dried to constant weight at  $150^{\circ}$  and analyzed.

*Anal.* Subs., 0.1571, 0.2316:  $Na_2SO_4$ , 0.0232, 0.0337. Calcd. for  $C_{20}H_7O_5Cl_4Na$ : Na, 4.68. Found: 4.78, 4.71.

The monosodium salt is only slightly soluble in water, but the presence of a little alkali or ammonia in the water causes it to dissolve with development of a blue color. The recrystallized product is brown and is not well crystallized. It does not melt when heated to  $300^{\circ}$ .

**DISODIUM SALT.**—Ten g. of the dihydroxy-tetrachlorofluoran was treated with 2 g. of sodium in ethanol in the same manner that was described for the monohydroxy-tetrachlorofluoran. The product that crystallizes from ethanol is grayish-brown. It loses very little weight when heated at  $140^{\circ}$  and does not melt when heated to  $300^{\circ}$ . It dissolves in the same solvents as the monosodium salt and gives the same blue color in dilute alkalis and ammonia solutions.

*Anal.* Subs., 0.2572, 0.1974:  $Na_2SO_4$ , 0.0701, 0.0541. Calcd. for  $C_{20}H_6O_5Cl_4Na_2$ : Na, 8.95. Found: 8.82, 8.87.

**MONOBROMO DERIVATIVE.**—Ten g. of the dihydroxy-tetrachlorofluoran was suspended in 150 cc. of glacial acetic acid and a slight excess of bromine over that calculated for the formation of a tribromo derivative was added. The compound was worked up in much the same manner as was 2,4-dibromo-3-hydroxy-tetrachlorofluoran. The crystals from benzene lost little weight when heated in carbon dioxide at  $150^{\circ}$ , nor did they melt when heated to  $300^{\circ}$ .

*Anal.* Subs., 0.1165, 0.1285:  $AgCl + AgBr$ , 0.1594, 0.1760: cc. of 0.1 *N*  $AgNO_3$ , 10.5, 11.55. Calcd. for  $C_{20}H_7O_5Cl_4Br$ : Cl, 25.84; Br, 14.55. Found: Cl, 25.82, 25.40; Br, 13.7, 14.43.

If the acetic acid filtrate from the crude monobromo derivative is poured into water, a grayish precipitate is secured which contains only a small percentage of bromine. It is



probably an oxidation product of the dihydroxy-tetrachlorofluoran, since it alone results when a large excess of bromine is used during the bromination. The monobromo derivative dissolves in concd. sulfuric acid with development of a red color, and in dilute alkalis with formation of a deep blue color. It remains colorless up to and including a *PH* value of 3.2. From *PH* 3.6 to 8.4 it is pink, and the blue color develops at *PH* 8.8. The compound is soluble in benzene, acetone and ethanol; slightly soluble in glacial acetic acid, and insoluble in water.

**Diacetate of 2-Bromo-3,4-dihydroxy-tetrachlorofluoran.**—Three g. of the monobromo derivative was converted to the acetate in the usual way. The crude material was dissolved in benzene, decolorized with bone black and allowed to crystallize from this solvent. The crystals hold one-half a molecule of benzene; m. p., 268–270°, with some decomposition.

*Anal.* Subs., 0.3738: loss at 140°, 0.0235. Calcd. for  $C_{20}H_5O_5Cl_4Br(COCH_3)_2 + 0.5 C_6H_6$ :  $C_6H_6$ , 5.81. Found: 6.29.

Subs. (heated at 140°), 0.1316, 0.1172:  $AgCl + AgBr$ , 0.1574, 0.1401; cc. of 0.1 *N*  $AgNO_3$ , 10.4, 9.25. Calcd. for  $C_{20}H_5O_5Cl_4Br(COCH_3)_2$ :  $Cl$ , 22.41;  $Br$ , 12.63. Found:  $Cl$ , 22.75, 23.0;  $Br$ , 11.75, 11.55.

The diacetate is quite slowly hydrolyzed by dilute aqueous alkalis and by concd. sulfuric acid. It is very soluble in acetone and benzene, and dissolves also in ethanol, glacial acetic acid and ether.

**Action of Dry Ammonia Gas on the Hydroxy-tetrachlorofluorans and their Bromo Derivatives.**—Small samples of the four compounds were placed in porcelain boats and heated to constant weight at 130°. The samples were then transferred to a combustion tube through which a slow current of dry ammonia gas was being passed. The ammonia was dried first by soda lime and then by sodium wire. The results are given in Table I.

TABLE I  
ABSORPTION OF DRY AMMONIA

	Subs., g.	$NH_3$ absorbed	$NH_3$ , %	Mols. of $NH_3$	Color
$C_{20}H_5O_4Cl_4$	0.2368	0.0009	0.38	0	Yellow
$C_{20}H_5O_4Cl_4Br_2$	.5278	.0150	2.76	1	Orange-yellow
$C_{20}H_5O_5Cl_4$	.2000	.0089	4.26	1.22	Dark brown
$C_{20}H_7O_5Cl_4Br$	.4842	.0410	7.80	2.74	Blue-black

In each case the color appeared immediately upon admitting the ammonia gas, but the gain in weight was slow, the samples taking from six to eight hours to reach constant weight. The absorbed ammonia is readily lost when the samples are heated in a current of dry air at 130° and the original weights of almost colorless compounds are secured. The relatively greater absorption of ammonia gas in the bromo derivatives demonstrates the acidifying influence of the bromine atoms.

### Summary

1. *3-Hydroxy-tetrachlorofluoran*, and *3,4-dihydroxy-tetrachlorofluoran* have been prepared from the "intermediate acid" (*o*-hydroxybenzoyl-tetrachloro-*o*-benzoic acid) and resorcinol and pyrogallol, respectively. Like the symmetrical phthaleins, they are tautomeric.

2. These hydroxy-tetrachlorofluorans are colorless as are also their

acetates and benzoates. These *colorless* compounds are therefore given the *lactoid* structure.

3. These hydroxy-tetrachlorofluorans, however, form *colored* sodium, ammonium and barium salts which are given the *quinoid* structure.

4. *2,4-Dibromo-3-hydroxy-tetrachlorofluoran*, and *2-bromo-3,4-dihydroxy-tetrachlorofluoran* have been prepared from the corresponding hydroxy-tetrachlorofluorans. They are *colorless* and form *colorless* acetates. However, they also are tautomeric, since they absorb ammonia gas and dissolve in alkalis with the development of color.

5. *3-Hydroxy-tetrachloro-hydrofluoranic acid* has been prepared by the reduction of the corresponding hydroxytetrachloro-fluoran. This acid and its acetate are *colorless* and dissolve in alkalis without development of color.

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[CONTRIBUTION FROM THE FIRESTONE TIRE AND RUBBER COMPANY]

## AN IMPROVEMENT IN MACMULLIN'S AUTOMATIC APPARATUS FOR DETERMINING THE MELTING POINTS OF ORGANIC COMPOUNDS

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RECEIVED JUNE 3, 1926

PUBLISHED AUGUST 5, 1926

In studying MacMullin's description and operation of an automatic melting-point apparatus<sup>1</sup> it was concluded that any errors arising from lag in temperature could be eliminated by employing an automatic device that would remove the maximum thermometer from the bath at the instant the substance melted, and thereby improve the accuracy of the apparatus and decrease the time required for a determination.

With this idea in mind the MacMullin apparatus was modified in such a way that when the substance melted and shut off the heating circuit, it also started a motor which removed the thermometer from the bath. When the thermometer was withdrawn the motor was automatically shut off, thereby raising the thermometer to a definite height and eliminating any possibility of breaking it.

**Apparatus.**—Referring to Fig. 1, A represents the maximum thermometer, B the mercury bath, C the pulley over which the cord supporting the thermometer passes, D the point of attachment of the thermometer cord on Disk F (diameter = 10 cm.), E the point of attachment of the switch cord on Disk G (diameter = 5.6 cm.), H the motor (an ordinary fan motor, J the throw arm of the single-pole single-throw switch K, L the relay, M the 110-volt power line and N the connections to the coil posts of the relay of the MacMullin apparatus. The disks may be made of Beaver Board,

<sup>1</sup> MacMullin, *THIS JOURNAL*, **48**, 439 (1926).