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

HYDROXYHYDROQUINOLSULFONEPHTHALEIN, 2',4',5'-TRIHYDROXYBENZOYLBENZENE-ORTHO-SULFONIC ACID (THE INTERMEDIATE ACID) AND SOME OF THEIR DERIVATIVES

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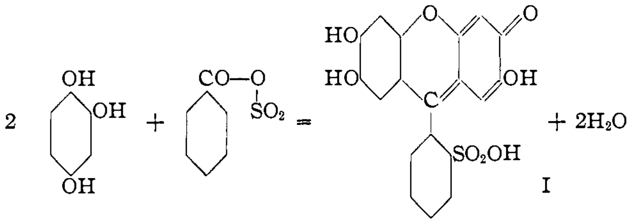
In 1900 Liebermann[2] and in 1901 Thiele and Jaeger[3] prepared hydroxyhydroquinolphthalein (dihydroxyfluorescein) from hydroxyhydroquinol and phthalic anhydride. The constitution of hydroxyhydroquinolphthalein was investigated by Feuerstein and Dutoit.[4] Hydroxyhydroquinolbenzein, the mother substance, was prepared and studied by Liebermann and Lindenbaum[5] in 1904 and by Ghosh and Watson[6] in 1913. Osorovitz[7] condensed hydroxyhydroquinol with tetrachlorophthalic anhydride and obtained hydroxyhydroquinoltetrachlorophthalein.

The reaction between hydroxyhydroquinol and *o*-sulfobenzoic anhydride is analogous to that of the phenols as a class with phthalic anhydride to form various phthaleins.



I

Analysis of the hydroxyhydroquinolsulfonephthalein shows that its composition corresponds to that of the pyrone ring structure and the fact that its alkaline solution is quite fluorescent indicates that it is 2,7-dihydroxysulfonefluorescein (I).

Like other sulfonephthaleins which have been studied, it is tautomeric and gives colored derivatives of the quinoid form and colorless derivatives of the lactoid form. Since the sulfonephthalein itself is highly colored, it has been assigned the quinoid formula and is presumably an inner carbonium or oxonium salt. The crystalline product contains about

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[1] From a dissertation presented by Mary L. Willard to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Liebermann, *Ber.*, **34**, 2299 (1901).

[3] Thiele and Jaeger, *ibid.*, **34**, 2617 (1901).

[4] Feuerstein and Dutoit, *ibid.*, **34**, 2637 (1901).

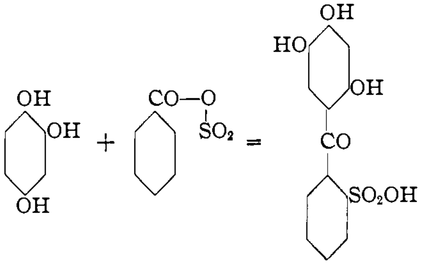
[5] Liebermann and Lindenbaum, *ibid.*, **37**, 1171 (1904).

[6] Ghosh and Watson, *Proc. Chem. Soc.*, **29**, 9 (1913).

[7] Osorovitz, *Ber.*, **36**, 1076 (1903).

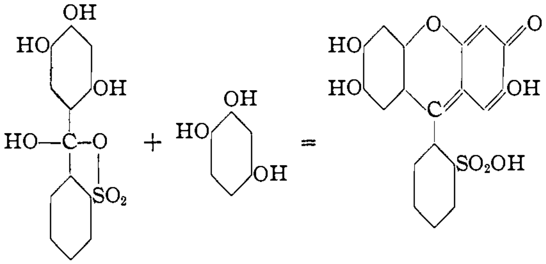
one-half a molecule of water per molecule of substance and is probably a solid solution of the quinoid, inner oxonium or carbonium salt, and the quinoid hydrate.

The formation of hydroxyhydroquinolsulfonephthalein takes place through an intermediate step, in a manner similar to that observed with other sulfonephthaleins which have been prepared in this Laboratory. A tautomeric substance, 2′,4′,5′-trihydroxybenzoylbenzene-*o*-sulfonic acid, which is called the intermediate acid, is obtained by the action of one molecule of *o*-sulfobenzoic anhydride upon one molecule of hydroxyhydroquinol.



II

The second step in the formation of hydroxyhydroquinolsulfonephthalein is the condensation of 2′,4′,5′-trihydroxybenzoylbenzene-2-sulfonic acid (II) with a second molecule of hydroxyhydroquinol with the elimination of water (III).



III

+ $2H_2O$

That the intermediate acid is a tautomeric, γ-ketonic acid is proved by preparing derivatives of both the ketone and lactone forms.

Hydroxyhydroquinolsulfonephthalein forms colored ethers, to which are assigned the quinoid structure.

Dibromohydroxyhydroquinolsulfonephthalein was isolated as a colored derivative which is also tautomeric. Since this dibromo derivative and its ammonium salt are colored, they are assigned the quinoid structure, while its tetra-acetate, which is colorless, is formulated as a derivative of the lactoid structure.

Concentrated sulfuric acid removes one molecule of water from the hydroxyhydroquinolsulfonephthalein, forming a violet-colored compound with a green luster, which has been given the name sulfoneviolein.

Hydroxyhydroquinolsulfonephthalein can be reduced with zinc dust, in formic acid solution, to hydroxyhydroquinolsulfonephthalin. The tetra-acetate of hydroxyhydroquinolsulfonephthalin and its silver salt have been prepared.

Experimental Part

In all calculations, 1925 atomic weights[8] were used. Carbon and hydrogen were determined by the usual combustion method with modifications of de Rhode for the presence of sulfur. Sulfur analyses were made in some cases with the Parr bomb, while in others Liebig's method of fusion with sulfur-free potassium nitrate and potassium hydroxide was used. Methoxyl and ethoxyl groups were determined by a modification of the Zeisel method.[9] Dennis' modification[10] of the Thiele apparatus was used to determine the melting points, which were uncorrected. A Bureau of Standards thermometer was used which was calibrated in 0.2°. In drying a substance to constant weight, an electrically heated tube[11] was used, through which was passed a slow current of dry air or carbon dioxide. The substance was introduced into this tube in a platinum boat on an asbestos support to prevent overheating by direct contact with the glass. The solubility of all salts was determined and classified according to Mulliken.[12]

All crystallographic data recorded were supplied by Professor Gill of the Department of Geology.

Preparation of Hydroxyhydroquinol.—Hydroxyhydroquinol was prepared from hydroquinol by oxidation to *p*-benzoquinone[13] with sodium dichromate in sulfuric acid solution and conversion of the latter into hydroxyhydroquinol tri-acetate according to a modification[14] of Thiele's method.[15]

The hydroxyhydroquinol tri-acetate was then hydrolyzed to hydroxyhydroquinol in the presence of hydrochloric acid.

2′,4′,5′-Trihydroxybenzoylbenzene-2-sulfonic Acid.—One hundred g. of hydroxyhydroquinol and 36 g. of *o*-sulfobenzoic anhydride[16] were heated at 100° for eight hours. The orange-red mass was powdered and treated with distilled water. It was filtered

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[8] G. P. Baxter, THIS JOURNAL, **47**, 600 (1925).

[9] Hewitt and Moore, *J. Chem. Soc.*, **81**, 318 (1902); Hewitt and Jones, *ibid.*, **115**, 193 (1919).

[10] Dennis, *J. Ind. Eng. Chem.*, **12**, 366 (1920).

[11] Chamot and Pratt, THIS JOURNAL, **32**, 635 (1910); Orndorff and Nichols, *Am. Chem. J.*, **48**, 477 (1912).

[12] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, **1908**, Vol. I, p. 38.

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II, p. 85.

[14] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1924**, Vol. IV, p. 35.

[15] Thiele, *Ber.*, **31**, 1248 (1898).

[16] Cobb, *Am. Chem. J.*, **35**, 502 (1906); White and Acree, THIS JOURNAL, **41**, 1197 (1919). The saccharin used in this work was furnished gratis by the Monsanto Chemical Works, St. Louis, Mo.

to remove the insoluble material, hydroxyhydroquinolsulfonephthalein. The filtrate was repeatedly boiled with bone black and filtered until the solution became colorless. The solution was carefully concentrated to about 100 cc. and 50 cc. of concentrated hydrochloric acid was added. The intermediate acid separated in small colorless crystals.

Anal. Calcd. for $C_{13}H_{10}O_7S{\cdot}2H_2O$: H_2O, 10.40. Found: H_2O, 10.52, 10.44. Calcd. for $C_{13}H_{10}O_7S$: mol. wt., 346.47; S, 10.34; C, 50.30; H, 3.25. Found: (methyl red) mol. wt., 345.5, 346.9; (phenolphthalein) mol. wt., 346.2, 346.8; S, 10.10, 10.45; C, 50.49, 50.81; H, 3.29, 3.24.

"Crystals of tabular, to thin, platey habitus reach a length of more than 2 mm. but are not perfect enough for gonimetric measurement. They are rhomboidal in shape, when well formed, and are certainly triclinic since extinction is not symmetrical and the bisectrix seen in converging polarized light is not normal to the surface of the plates. Double refraction is rather high and dispersion is strong."

The intermediate acid could also be separated from the fusion filtrate by precipitation of the barium salt with barium carbonate and subsequent acidification. The intermediate acid is very soluble in water; soluble in methanol, ethanol, acetone, ether and glacial acetic acid. It is difficultly soluble in benzene, xylene, petroleum ether and chloroform. The structure of the intermediate acid was proved by the method of Orndorff and Cornwell,[17] by fusion with potassium hydroxide at 210° for two hours. From the fused mass, after crystallization from 50% alcohol, small needles melting at 210° were obtained. This substance corresponded in properties to hydroxyhydroquinolcarboxylic acid (2′,4′,5′-trihydroxybenzoic acid).[18]

When 2′,4′,5′-trihydroxybenzoylbenzene-2-sulfonic acid was heated for three hours at 140°, it decomposed, forming hydroxyhydroquinolsulfonephthalein and *o*-sulfobenzoic anhydride. The intermediate acid reacted under similar conditions with hydroxyhydroquinol to form hydroxyhydroquinolsulfonephthalein. Several derivatives of the tautomeric forms of the intermediate acid (**2′,4′,5′-trihydroxybenzoylbenzene-2-sulfonic acid**) were made.

Ammonium Salt.[19]—Twenty-two g. of the acid ammonium salt of *o*-sulfobenzoic acid was heated with 12 g. of hydroxyhydroquinol at 190–195° for five hours. The fused mass was dissolved in hot water and recrystallized three times from hot water. The ammonium salt is very soluble in water, methanol or ethanol. It is insoluble in benzene, ether or petroleum ether.

Barium Salt.—Ten g. of the pure intermediate acid was boiled with 30 g. of barium carbonate for one hour. After the solution had been filtered, the barium salt of the intermediate acid crystallized from the concentrated filtrate. It was recrystallized

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[17] Orndorff and Cornwell, This Journal, **48**, 986 (1926).

[18] Thiele and Jaeger, *Ber.*, **34**, 2840 (1901).

[19] Analyses of the following compounds can be found in the thesis in the Library, Cornell University, Ithaca, New York.

twice from hot water. The barium salt is easily soluble in water, methanol and ethanol but very difficultly soluble in other organic solvents.

Zinc Salt.—Five g. of the pure intermediate acid was boiled with 25 g. of zinc carbonate for one hour. The excess of zinc carbonate was removed by filtration and the filtrate was concentrated almost to dryness, when plate-like crystals separated which were recrystallized once from water. The colorless zinc salt crystallized with 5 molecules of water of crystallization. The zinc salt is soluble in water, methanol and ethanol but difficultly soluble in other organic solvents.

Tetra-sodium Salt.—Five g. of the pure intermediate acid was treated with the calculated amount of 0.1 *N* sodium hydroxide. The solution was evaporated to dryness and the salt recrystallized from water. The sodium salt is very soluble in water, methanol and ethanol. It is insoluble in ether, benzene and xylene.

Tetra-acetate.—Ten g. of pure dry intermediate acid was boiled with 100 cc. of acetic anhydride for three hours. The solution was filtered and about 50 cc. of acetic anhydride was distilled from the filtrate. Upon standing for twelve hours the colorless crystals separated from the solution. These were recrystallized twice from anhydrous ether. The tetra-acetate is soluble in ether and acetone but insoluble in benzene and petroleum ether. It is slowly hydrolyzed by long heating with water or alcohol.

Preparation of Hydroxyhydroquinolsulfonephthalein

(1) From the Anhydride of *o*-Sulfobenzoic Acid and Hydroxyhydroquinol Triacetate.—Hydroxyhydroquinolsulfonephthalein was prepared in the best yields by heating 200 g. of hydroxyhydroquinol tri-acetate with 70 g. of *o*-sulfobenzoic anhydride for eight hours at 140°. The last traces of acetic acid were removed by the use of reduced pressure. The mass, consisting of tiny green crystals, was purified by dissolving it in hot dilute sodium hydroxide and acidifying with dilute hydrochloric acid. The yield was 80%.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, 2.20. Found: 2.16, 2.28. Calcd. for $C_{19}H_{12}O_8S$: S, 8.01. Found: S, 7.94, 7.97.

(2) From the Chlorides of *o*-Sulfobenzoic Acid and Hydroxyhydroquinol.—Twenty-four g. of *o*-sulfobenzoic acid chloride and 28 g. of hydroxyhydroquinol were heated for three hours on a steam-bath and three hours more at 120°, using reduced pressure during the last hour. The product was purified as before. The yield was 40%. A small amount of material was insoluble in sodium hydroxide which was probably, if analogous to other sulfonephthaleins, the ester of *o*-sulfobenzoic acid.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, 2.20. Found: 2.12, 2.16. Calcd. for $C_{19}H_{12}O_8S$: C, 56.97; H, 3.02; S, 8.01. Found: C, 56.97, 56.53; H, 3.10, 3.09; S, 8.03, 7.86.

(3) From the Anhydride of *o*-Sulfobenzoic Acid and Hydroxyhydroquinol.—Eighteen g. of *o*-sulfobenzoic anhydride and 28 g. of hydroxyhydroquinol were heated at 130° for thirty hours. The product was purified as before. If a temperature higher than 130° was used, tar was formed; if lower, the yield rapidly decreased. The yield was 30%.

Anal. Calcd. for $C_{19}H_{12}O_8S \cdot {}^1/_2H_2O$: H_2O, 2.20. Found: 2.17, 2.08. Calcd. for $C_{19}H_{12}O_8S$: S, 8.01. Found: S, 7.46, 7.52.

When anhydrous zinc chloride was used as a condensation agent, the yield was reduced to 15%.

Properties and Crystalline Form.—Professor Gill examined crystals of hydroxyhydroquinolsulfonephthalein prepared by fusion of the chlorides of *o*-sulfobenzoic acid and hydroxyhydroquinol. He stated: "The crystalline aggregates show bright yellow-green surface color, but do not have sufficiently sharp crystal boundaries to permit determination of the crystal system. They are nearly opaque except in very fine powder, when they appear to transmit a little reddish-brown colored light."

The green crystals of hydroxyhydroquinolsulfonephthalein, when ground in an agate mortar, formed a reddish-orange powder. Hydroxyhydroquinolsulfonephthalein is difficultly soluble in water, forming a red solution with green fluorescence. It is soluble in dilute (2%) sodium hydroxide, forming a red solution with green fluorescence. With concentrated (30%) sodium hydroxide, a fuchsin-colored solution is obtained. Concentrated sulfuric acid forms a yellow solution which is not fluorescent. Hydroxyhydroquinolsulfonephthalein is soluble in methanol, ethanol, acetic acid and acetone. It is insoluble in benzene, toluene, ether and petroleum ether. It can be precipitated from cold dilute alkaline solutions with dilute acid as a reddish powder and from hot solutions as fine green crystals. The *P*H was determined by Clark's colorimetric method[20] using a color chart found in Mulliken.[21] There was a change from OY to R at 7.2 and from VR to RV at 12.0.

The following derivatives of the tautomeric forms of **hydroxyhydroquinolsulfonephthalein** were made.

Ammonium Salt.—Samples of pure dry hydroxyhydroquinolsulfonephthalein absorbed 4 molecules of ammonia gas, a bluish-brown powder resulting, the aqueous solutions of which were fuchsin colored. When the tetra-ammonium salt was allowed to stand in an evacuated desiccator over sulfuric acid, a red stable mono-ammonium salt resulted. Hydrogen chloride gas did not form a stable compound with hydroxyhydroquinolsulfonephthalein.

Barium Salt.—Five g. of hydroxyhydroquinolsulfonephthalein and 30 g. of barium carbonate were boiled with 3 liters of water until all the sulfonephthalein had dissolved. After filtration and concentration of the filtrate, red crystals separated. The barium salt is very soluble in water, methanol and ethanol. It can be hydrolyzed with concentrated hydrochloric acid to the sulfonephthalein.

Zinc Salt.—An aqueous suspension of pure hydroxyhydroquinolsulfonephthalein was boiled with zinc dust until the solution became bright orange in color. After filtration, concentration and recrystallization from water, orange-red crystals were obtained. The zinc salt is soluble in water, methanol, ethanol and butanol.

Potassium Salt.—A sample of pure hydroxyhydroquinolsulfonephthalein was dissolved in the calculated amount of potassium hydroxide solution. The solution was filtered and the filtrate was concentrated. Reddish crystals separated. The potassium salt is readily soluble in most organic solvents.

Tetra-acetate.—A sample of pure dry hydroxyhydroquinolsulfonephthalein was heated for one hour with excess acetic anhydride. After solution had taken place,

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[20] Clark, "The Determination of H-Ion Concentration," Williams and Wilkins Company, Baltimore, Maryland, **1922**.

[21] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1908**, Vol. 1.

about one-half the solvent was distilled off. Brownish-yellow needles separated from the remaining solution upon cooling. After three recrystallizations from acetic anhydride, colorless needles were obtained. The tetra-acetate was slowly hydrolyzed with water and more rapidly hydrolyzed with alkalies.

Tetra-benzoate.—A sample of pure dry hydroxyhydroquinolsulfonephthalein was boiled with excess benzoyl chloride for five hours. It was filtered and the filtrate was evaporated to dryness; the residue was extracted with hot benzene. The benzene extracts were concentrated in the presence of a little bone black. From the filtered suspension, small crystals separated upon cooling. They were twice recrystallized from benzene. The colorless tetra-benzoate is soluble in methanol, ethanol, ether, toluene, benzene and xylene. It is readily saponified with dilute sodium hydroxide and also boiling ethanol.

Sodium Salt of Trimethyl Ether.—Twenty g. of pure dry hydroxyhydroquinolsulfonephthalein was treated with methyl iodide and sodium methylate according to Claissen's method as used by Orndorff and Fuchs[22] in the preparation of pyrogallolsulfonephthalein and sulfonegallein ethers. About 20 g. of a dry green powder was obtained from the ether. The green powder was extracted with acetone. The acetone extracts were assembled and concentrated and a few red crystals were obtained which were recrystallized from acetone.

Anal. Calcd. for $C_{19}H_8O_5SNa(OCH_3)_3$: Na, 4.95; CH_3O, 20.05. Found: Na, 5.07, 5.07; CH_3O, 20.05, 20.17.

The sodium salt is easily soluble in most organic solvents. It does not form a blue solution with sodium hydroxide since the hydroxyl positions are already occupied and do not permit the formation of poly salts.

Trimethyl Ether.—The material left undissolved after the acetone extractions was dissolved in water and reprecipitated with hydrochloric acid. It was dried and extracted with boiling glacial acetic acid. The extractions were concentrated and a few reddish crystals were obtained which were recrystallized from methanol.

Anal. Calcd. for $C_{22}H_{18}O_8S$: S, 7.25. Found: S, 7.40, 7.50.

The trimethyl ether of hydroxyhydroquinolsulfonephthalein is soluble in most solvents except benzene and ether.

Dimethyl Ether.—The reddish material left undissolved after the extraction with boiling acetic acid was recrystallized four times from methanol.

Anal. Calcd. for $C_{19}H_{10}OS(OCH_3)_3$: CH_3O, 14.49. Found: CH_3O, 14.39, 14.28.

The dimethyl ether is soluble in water, methanol and ethanol. It is insoluble in ether, acetic acid, benzene and toluene.

Aniline Salt.—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 200 cc. of aniline on a steam-bath. The solution was then heated for twelve hours at 120°. When the solution was cooled red needles separated. The crystals were filtered off and washed with ether. They did not melt below 300°.

> "The dark reddish spongy masses appear to be made up of very small crystals, not more than 0.002 or 0.003 mm. in diameter. Nothing could be determined further than that the sparkling reflection from the surface indicated crystalline character."

Anal. Calcd. for $C_{19}H_{12}O_8S(C_6H_5NH_2)$: S, 6.50. Found: S, 6.38, 6.46.

The red aniline salt is soluble in hot water and methanol. Aniline was liberated when the salt was treated with sodium hydroxide.

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[22] Orndorff and Fuchs, THIS JOURNAL, **48**, 1939 (1926).

Dibromohydroxyhydroquinolsulfonephthalein.—No reaction was observed between bromine and hydroxyhydroquinolsulfonephthalein in glacial acetic acid solution. Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 300 cc. of absolute ethanol and 20 g. of bromine in 100 cc. of absolute ethanol added. The solution was heated on a steam-bath for eight hours. When it had cooled green crystals separated which were purified by dissolving in water and precipitating with hydrochloric acid.

Anal. Calcd. for $C_{19}H_{10}O_8Br_2S \cdot 2^1/_2H_2O$: H_2O, 7.48. Found: H_2O, 7.48, 6.90. Calcd. for $C_{19}H_{10}O_8Br_2S$: S, 5.75; Br, 28.65. Found: S, 5.82, 5.92; Br, 28.46, 28.20.

The dibromo derivative was soluble in water. It dissolved in dilute sodium hydroxide forming a red solution or a blue solution with more concentrated alkali. A color change was noted at *P*H 6.4 from RO to VR.

Action of **Ammonia.**—Several samples of pure dry dibromohydroxyhydroquinolsulfonephthalein, when exposed to a stream of dry ammonia, absorbed 5.5 molecules of ammonia. After standing over sulfuric acid for some time a stable tri-ammonium salt resulted.

Tetra-acetate.—Ten g. of pure dry dibromohydroxyhydroquinolsulfonephthalein was boiled with 100 cc. of acetic anhydride for one hour. The solution was filtered into ice water. A brownish solid separated upon standing, which was purified by repeated recrystallization from benzene using bone black. This salt is very easily hydrolyzed with alkalies or water. It is soluble in benzene.

Sulfoneviolein.—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 10 cc. of concentrated sulfuric acid. The solution was heated for twelve hours at 120°. It was cooled and poured into ice water; a brownish-blue solid separated. It acquired a green luster upon drying and was recrystallized from nitrobenzene as fine green crystals.

Anal. Calcd. for $C_{19}H_{10}O_7S$: S, 8.39. Found: S, 8.46, 8.45.

It was insoluble in most organic solvents. It was slightly soluble in ethanol to a brown solution. It was soluble in acids to a red solution but was insoluble in alkalies.

Hydroxyhydroquinolsulfonephthalein.—Five g. of hydroxyhydroquinolsulfonephthalein was dissolved in about 200 cc. of formic acid. The solution was boiled with 10 g. of zinc dust. After about fifteen minutes it was completely decolorized. It was filtered in the presence of carbon dioxide. Upon cooling minute colorless crystals separated which were recrystallized from 50% formic acid.

Anal. Calcd. for $C_{19}H_{14}O_8S$: S, 7.97. Found: S, 8.22, 8.03.

"This substance is ocher yellow in mass, and a few of the larger crystals show pleochroism from buff to colorless. It is composed of sharply defined crystals, mostly 0.01 to 0.03 mm. in diameter. These have rather low double refraction and oblique extinction. The shape would seem to be monoclinic, though they may be triclinic."

The reduction product is soluble in most organic solvents. It oxidizes readily and becomes red upon standing in the air.

Tetra-acetate.—Ten g. of pure dry hydroxyhydroquinolsulfonephthalein was dissolved in 200 cc. of glacial acetic acid. Five g. of zinc dust and a few drops of copper sulfate (10%) solution were added. The mixture was boiled on a sand-bath for three hours. The acetic acid solution was filtered, concentrated to half the original volume and poured into ice water. A nearly colorless precipitate separated which was crystallized from 95% ethanol. The tetra-acetate of the reduction product was difficultly soluble in methanol, ethanol, benzene and acetone.

Anal. Calcd. for $C_{27}H_{22}O_{12}S$: S, 5.61. Found: S, 5.66.

Silver Salt of Tetra-acetate.—Five g. of hydroxyhydroquinolsulfonephthalein tetra-acetate dissolved in 200 cc. of absolute ethanol was added to 25 g. of silver nitrate dissolved in this alcohol, which had been previously boiled with other silver nitrate for one hour. After a few minutes' standing, fine colorless crystals separated. They were filtered off and allowed to dry in the absence of light. The silver salt was soluble in methanol and benzene but insoluble in most organic solvents.

Summary

1. 2′,4′,5′-Trihydroxybenzoylbenzene-2-sulfonic acid has been prepared. It has been shown that it is the intermediate step in the preparation of hydroxyhydroquinolsulfonephthalein. This intermediate acid is a γ-ketonic acid and acts as a tautomeric substance, giving derivatives of the ketone form and of the lactone form.

2. The preparation and properties of pure hydroxyhydroquinolsulfonephthalein have been studied. The best results were obtained by the condensation of hydroxyhydroquinol tri-acetate and *o*-sulfobenzoic anhydride. The product is dihydroxysulfonefluorescein formed by elimination of a molecule of water, with the production of a pyrone ring. Dilute alkaline solutions are fluorescent.

3. Since hydroxyhydroquinolsulfonephthalein is a highly-colored substance, it is represented as having the quinoid structure. It is tautomeric and yields colorless derivatives of the lactoid modification, as the tetra-acetate and tetra-benzoate, and colored derivatives of the quinoid structure, as the barium, zinc or potassium salts.

4. Colored di- and trimethyl ethers of hydroxyhydroquinolsulfonephthalein have been prepared, both of which are assigned the quinoid structure.

5. Dibromohydroxyhydroquinolsulfonephthalein and its ammonium salt were obtained as colored substances, to which the quinoid structure is assigned. The colorless tetra-acetate is considered to be a derivative of the lactoid structure.

6. Sulfuric acid removes a molecule of water from hydroxyhydroquinolsulfonephthalein, forming sulfoneviolein.

7. Hydroxyhydroquinolsulfonephthalin, the reduction product of hydroxyhydroquinolsulfonephthalein, its tetra-acetate and the silver salt of the tetra-acetate have been prepared. They are colorless and are easily oxidized.

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