

The luminescence of unsaturated compounds was used to throw additional light on the structure of pyrromagnesium iodide.

3. The reaction between pyrrolidine and methylmagnesium iodide has been studied. It has been shown that the $-\text{MgX}$ group does not migrate to the alpha position under the experimental conditions studied.

4. The synthesis of the α -dithionic acid of pyrrole is described.

BERKELEY, CALIFORNIA

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

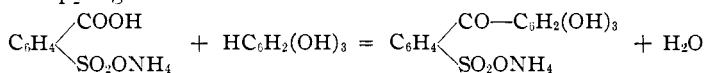
PYROGALLOLSULFONEPHTHALEIN, SULFONEGALLEIN, 2,3,4-TRIHYDROXY-BENZOYL-BENZENE-ORTHO-SULFONIC ACID (THE INTERMEDIATE ACID), AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND NATHANIEL FUCHS¹

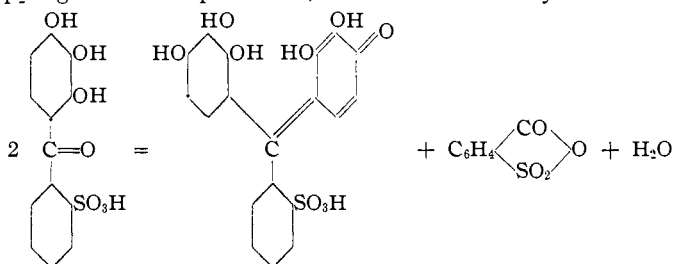
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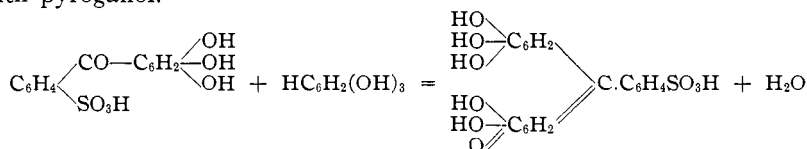
The ammonium salt of 2,3,4-trihydroxy-benzoyl-benzene-*o*-sulfonic acid was prepared by heating the acid ammonium salt of *o*-sulfobenzoic acid with pyrogallol.



The free acid was obtained by passing dry hydrogen chloride into the ammonium salt suspended in absolute ethanol. When heated alone at 140° , it forms pyrogallolsulfonephthalein, *o*-sulfobenzoic anhydride and water.



Pyrogallolsulfonephthalein also results when the trihydroxy acid is heated with pyrogallol.

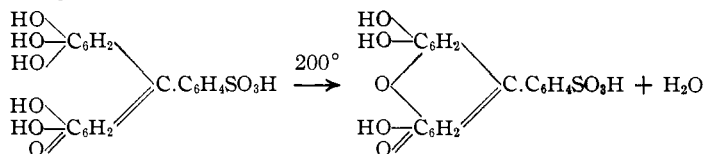


¹ This article is based on a thesis submitted to the Faculty of the Graduate School of Cornell University by Nathaniel Fuchs, Grasselli Fellow in Chemistry, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. An abstract of this paper was presented at the seventieth meeting of the American Chemical Society at Los Angeles, in 1925.

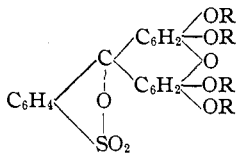
Hence the trihydroxy acid is called the intermediate acid. Pyrogallol-sulfonephthalein is best made by heating *o*-sulfobenzoic acid anhydride with pyrogallol at 135–140°, with zinc chloride. The reaction takes place in two steps: first one molecule of pyrogallol combines with one of the anhydride to give the trihydroxy acid, and then this acid reacts with more pyrogallol to form the sulfonephthalein as shown above. The sulfonephthalein was also obtained by heating pyrogallol with saccharin and sulfuric acid, or with the chlorides of *o*-sulfobenzoic acid.

Pyrogallolsulfonephthalein reacts as a tautomeric substance, forming colored, *quinoid* and colorless *lactoid* derivatives. The compound itself is colored, has the *quinoid* form and is an inner carbonium or oxonium salt. As a monobasic acid it forms highly-colored salts. It also reacts as a polybasic acid as shown by the zinc and the lead salts.

When heated to 200° pyrogallolsulfonephthalein loses a molecule of water and gives sulfonegallein.



Sulfonegallein reverts to pyrogallolsulfonephthalein in the presence of moisture. When pyrogallolsulfonephthalein reacts with certain reagents, derivatives of *sulfonegallein* result. Thus when boiled with aniline, it gives the aniline salt of *sulfonegallein*. With acetic anhydride, it forms *sulfonegallein* tetracetate, and with benzoyl chloride *sulfonegallein* tetrabenzoate. These are colorless compounds and have the *lactoid* structure.



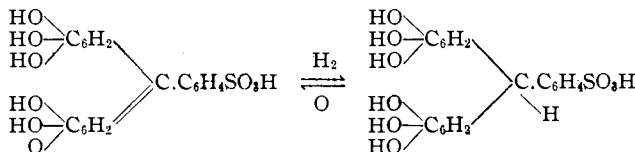
where R = COCH₃ or COC₆H₅

They are hydrolyzed by dilute alkalis, showing at first a green fluorescence, which is soon replaced by a blue color.

Pyrogallolsulfonephthalein forms a brick-red, monomethyl ether, and a red trimethyl ether. The dimethyl ether of *sulfonegallein* occurs in two modifications, one consisting of orange, rectangular tablets and the other of red, triangular plates. Both crystallize in the rhombic system. As all of these ethers are colored they have the *quinoid* structure.

Pyrogallolsulfonephthalein yields a colored dibromo derivative, which is also tautomeric, having for itself and its ammonium salt the *quinoid* structure, and forming a colorless tetrabenzoate of *dibromosulfonegallein* which has the *lactoid* structure.

On reduction with zinc dust and water, pyrogallolsulfonephthalein is converted into the colorless zinc salt of pyrogallolsulfonephthalin. Pyrogallolsulfonephthalin is very readily oxidized back to pyrogallolsulfonephthalein.



The sulfonephthalin differs from the sulfonephthalein in being readily soluble in water.

Experimental Part²

The Ammonium Salt of 2,3,4-Trihydroxy-benzoyl-benzene-*o*-sulfonic Acid.—Two hundred g. of the acid ammonium salt of *o*-sulfobenzoic acid³ was heated with 115 g. of pyrogallol. The fused mass, after being heated at 190–195° for an hour, became solid. Three crystallizations of the light orange-red product from hot water gave colorless prisms. The yield was 68%. Analyses⁴ of the air-dried crystals showed that they were the ammonium salt of trihydroxy-benzoyl-benzene-*o*-sulfonic acid with 0.25 molecule of water of crystallization.

Anal. Subs., 0.4807, 0.5971: loss at 120°, H₂O, 0.0065, 0.0082. Calcd. for C₁₃H₁₀O₇SNH₃ + 0.25 H₂O: H₂O, 1.36. Found: 1.35, 1.37.

Subs. (dry), 0.5555, 0.5555, 0.5971: cc. of 0.1 *N* H₂SO₄, 16.94, 16.75, 17.92. Subs. (dry), 0.5889: BaSO₄, 0.4120. Calcd. for C₁₃H₁₀O₇SNH₃: NH₃, 5.20; S, 9.80. Found: NH₃, 5.19, 5.14, 5.11; S, 9.61.

The ammonium salt is practically insoluble in most of the usual organic solvents, but dissolves somewhat in methanol and in ethanol and is very soluble in hot water. When heated in a melting-point tube, it begins to turn dark at 296° and melts sharply to a red liquid at 298°.

2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic Acid.—Fifty g. of the ammonium salt was suspended in 300 cc. of absolute ethanol. Dry hydrogen chloride was passed into the suspension for six hours. The ammonium salt of the trihydroxy acid dissolved and ammonium chloride was precipitated. The alcohol solution was filtered and concentrated, but no crystals could be obtained. When all the alcohol was removed, a sticky, brownish mass remained. This was thoroughly dried on the water-bath in a vacuum and then left in a vacuum desiccator for a few days. It crystallized slowly into a cream-colored solid. The material was powdered and recrystallized five times from concd. hydrochloric acid. In this way, light yellow crystals were obtained. They begin to soften at 103° and melt to a yellow-brown liquid at 108–109°. Analyses of the air-dried product showed that it was trihydroxy-benzoyl-benzene-*o*-sulfonic acid with 3 molecules of water of crystallization, but the water could not be determined by drying because the acid changed into pyrogallolsulfonephthalein, *o*-sulfobenzoic acid anhydride and water when heated.

Anal. Subs., 0.3562, 0.2966: BaSO₄, 0.2284, 0.1918. Calcd. for C₁₃H₁₀O₇S + 3H₂O: S, 8.80. Found: 8.81, 8.88.

² We are indebted to the Monsanto Chemical Works of St. Louis for the saccharin used in this investigation.

³ Blackshear, *Am. Chem. J.*, **14**, 455 (1892).

⁴ International Atomic Weights for 1925 are used in the computations in this paper.

The molecular weight of the acid with 3 molecules of water was determined by titration with 0.1 *N* sodium hydroxide solution. With methyl red it titrates as a *mono-basic acid*.

Mol. Wt. Subs., 0.2117, 0.5290: cc. of 0.1 *N* NaOH, 5.83, 14.46. Calcd. for $C_{13}H_{10}O_7S + 3H_2O$: mol. wt., 364.2. Found: 363.1, 365.8.

It titrates as a *dibasic acid*, however, with phenolphthalein.

Mol. Wt. Subs., 0.2117, 0.3640: cc. of 0.1 *N* NaOH, 11.61, 19.91. Calcd. for $C_{13}H_{10}O_7S + 3H_2O$: mol. wt., 364.2. Found: 364.7, 365.6.

The acid is very soluble in water, ethanol and ethyl acetate, and is practically insoluble in ether, benzene and chloroform.

TRIBENZOATE.—The benzoate was made by boiling the acid with benzoyl chloride. The excess of benzoyl chloride was evaporated in a current of carbon dioxide in a water oven. The product could not be crystallized, but was purified by dissolving it in ether and precipitating with petroleum ether. The colorless flocculent precipitate was precipitated twice again in the same way. The analysis below, made on the product after it had been kept in a vacuum desiccator for ten days, showed that it was the tribenzoate; m. p., 62–64°.

Anal. Subs., 0.4834: $BaSO_4$, 0.1845. Calcd. for $C_{13}H_7O_7S (COC_6H_5)_3$: S, 5.15. Found: 5.24.

Pyrogallolsulfonephthalein

Preparation of Pyrogallolsulfonephthalein. (1) *By Heating 2,3,4-Trihydroxybenzoyl-benzene-o-sulfonic Acid.*—Five g. of the pure acid was heated for six hours at 140°. The mass turned green and colorless needles of the anhydride of *o*-sulfobenzoic acid sublimed. The crystalline pyrogallolsulfonephthalein was recrystallized by dissolving it in hot, dil. sodium hydroxide solution and acidifying with hydrochloric acid. Two g. of green crystals was obtained. The material was dried at 130°.

Anal. Subs. (dry), 0.4362: $BaSO_4$, 0.2415. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found S, 7.60.

(2) *From 2,3,4-Trihydroxybenzoyl-benzene-o-sulfonic Acid and Pyrogallol.*—Five g. of the pure acid was heated with 2 g. of pyrogallol at 135–145°. The red liquid became a green solid after being heated for six hours. The sulfonephthalein was recrystallized as above. The air-dried sample was analyzed.

Anal. Subs., 0.3452: loss at 130°, 0.0021. *Subs. (dry)*, 0.3431: $BaSO_4$, 0.1904. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found: S, 7.62.

(3) *From the Anhydride of o-Sulfobenzoic Acid and Pyrogallol.*—Seventy-five g. of *o*-sulfobenzoic acid anhydride and 113 g. of pyrogallol were heated at 130–135° for 20 hours. The mixture was treated with hot water thrice and filtered. The finely-crystalline, reddish-brown sulfonephthalein had a green surface color; yield, 51%. The same yield was obtained by running a condensation at 135–140° for 18 hours or for 30 hours. By using zinc chloride and heating at 135–140°, the same yield was obtained, but the time required was reduced to eight hours and the product consisted of larger crystals much more easily purified. Pyrogallolsulfonephthalein is best made in this way.

The product was purified by dissolving in sodium hydroxide solution and precipitating with hydrochloric acid. A second recrystallization in the same way gave dark green crystals which ground to a red powder. They were allowed to dry in the air for a week and analyzed.

Anal. Subs., 0.2304, 0.2423; loss at 130°, 0.0017, 0.0019. *Subs. (dry)*, 0.2287, 0.2404: CO_2 , 0.4570, 0.4791; H_2O , 0.0715, 0.0747. *Subs. (dry)*, 0.5118, 0.6470; $BaSO_4$, 0.2806, 0.3594. Calcd. for $C_{19}H_{14}O_9S$: C, 54.52; H, 3.37; S, 7.67. Found: C, 54.50, 54.35; H, 3.50, 3.48; S, 7.53, 7.63.

These analyses prove that pyrogallolsulfonephthalein has the formula $C_{19}H_{14}O_9S$ and not $C_{19}H_{10}O_8S$ as stated by Sohon.⁵

(4) *From the Chlorides of o-Sulfobenzoic Acid and Pyrogallol.*—Ten g. of the chlorides and 13.5 g. of pyrogallol were heated six hours at 145°. Hydrogen chloride was given off. The product was dissolved in sodium hydroxide solution. The deep blue alkaline solution treated with hydrochloric acid gave 6 g. of green crystals of pyrogallolsulfonephthalein.

About 1 g. did not dissolve in the sodium hydroxide solution. When this substance was crystallized from benzene, colorless, transparent crystals, which melted at 109–111° and boiled in the melting point tube at about 230° were obtained. From analogy with the other esters of *o*-sulfobenzoic acid, which were obtained as by-products in the condensation of phenols with the chlorides of *o*-sulfobenzoic acid, it appears that the product is the *dipyrogallyl ester of o-sulfobenzoic acid*, $(OH)_2C_6H_3OCO.C_6H_4.SO_2OC_6H_3(OH)_2$.

(5) *From Saccharin, Sulfuric Acid and Pyrogallol.*—Twenty g. of saccharin, 25 g. of concd. sulfuric acid and 30 g. of pyrogallol were heated together at 135–145° for six hours. Water was added and the green crystals of pyrogallolsulfonephthalein recrystallized in the usual way; yield, 20%.

Anal. Subs. (dried at 130°), 0.5146; $BaSO_4$, 0.2856. Calcd. for $C_{19}H_{14}O_9S$: S, 7.67. Found: 7.62.

Properties and Crystalline Form.—Pyrogallolsulfonephthalein is insoluble in most organic solvents. It dissolves somewhat in water, methanol, ethanol and formic acid (85%) forming a red solution. In cold water it dissolves to the extent of one g. in about 20 liters and it is about three times as soluble in boiling water. Sodium hydroxide or sodium carbonate solutions dissolve it very readily, producing in very dilute solutions of the alkali a deep red color (monosodium salt) and in stronger solutions a very deep blue color (polysodium salt). Sodium bicarbonate solution gives only the deep red color of the monosodium salt. In very dilute aqueous ammonia solution a red color is obtained, changing to a purple as the concentration of ammonia is increased. Acids precipitate the pyrogallolsulfonephthalein from these solutions. The color changes at different hydrogen-ion concentrations are given in the table below. The colors were judged by comparison with the color chart found in Mulliken's "Identification of Pure Organic Compounds," Vol. 1.

P_H	2.0	3.0	4.0	5.0	6.0–10.0	11.0	12.0
Color	YO_1	YO_1	RO_1	R_1	VR_1	RV_1	VB_1

In alkaline solutions stronger than $P_H = 8$, the color fades rapidly due to oxidation. None of the solutions of pyrogallolsulfonephthalein show fluorescence.

Pyrogallolsulfonephthalein does not melt below 315°. It dissolves in concd. sulfuric acid forming a red solution and is precipitated in a red form when the solution is poured into water. Unlike pyrogallolbenzein,⁶ it does not absorb hydrogen chloride, indicating that pyrogallolsulfonephthalein should be represented as having the formula of an inner oxonium or inner carbonium salt.

Professor Vieweg of the Department of Geology of Cornell University described the crystals as follows.

"The crystals of pyrogallolsulfonephthalein from distilled water are bladed. They have a green metallic surface color, and, when powdered, an orange-yellow transmission color. There is no apparent difference between the crystals from dilute hydrochloric acid and those from water. The system of crystallization could not be determined."

⁵ Sohon, *Am. Chem. J.*, **20**, 257 (1898).

⁶ Orndorff and Wang, *THIS JOURNAL*, **47**, 290 (1925).

Pyrogallolsulfonephthalein crystallizes best from methanol. The glistening green crystals obtained were allowed to dry in the air and analyzed.

Anal. Subs., 0.4760, 0.1927, 0.3121: loss at 130°, H₂O, 0.0566, 0.0221, 0.0360. Subs. (dry), 0.4194: BaSO₄, 0.2317. Calcd. for C₁₉H₁₄O₈S + 3H₂O: H₂O, 11.45. Found: H₂O, 11.89, 11.47, 11.53. Calcd. for C₁₉H₁₄O₈S: S, 7.67. Found: S, 7.59.

The substance contains three molecules of water of crystallization, in spite of the fact that it crystallized from methanol.

Professor Vieweg described the crystals as follows. "This substance forms rhomboid tablets, having a green surface color. The crystallization is *rhombic*. Calling the face on which the crystals lie the basal pinacoid (001), the prism angles are found, by measurement with the microscope, to be 120°. The crystals are pleochroic. Parallel to the long diagonal of the rhombus, vibrations of a greenish-yellow color are transmitted; perpendicular to this, visible light is practically completely absorbed."

Conversion into Sulfonegallein.—When pyrogallolsulfonephthalein, dried at 130°, is heated to 200° for several hours, it loses one molecule of water of constitution. The original green or greenish-brown color changes to a bright red.

Anal. Subs. (dried at 130°), 0.4929, 0.2606, 0.2851: loss at 200°, 0.0195, 0.0110, 0.0119. Calcd. for C₁₉H₁₄O₈S: loss of 1 H₂O, 4.31. Found: 3.96, 4.22, 4.17.

The molecule of water is split off from the two hydroxyl groups in the pyrogallol residues in the *ortho* positions to the methane carbon atom, leaving the molecule with a pyrone ring. The reverse change takes place when the sulfonegallein is allowed to stand in the air. The bright red compound takes up the molecule of water lost on heating and regains its original green color.

Anal. Subs., dried at 200°, 0.2732: gain, H₂O, 0.0143. Calcd. for C₁₉H₁₄O₈S.H₂O: H₂O, 4.31. Found: 4.97.

Sulfonegallein conducts itself towards most reagents in exactly the same way that pyrogallolsulfonephthalein does.

A more stable form of sulfonegallein was made as follows. A solution of 5 g. of pure pyrogallolsulfonephthalein in a small volume of 2% sodium hydroxide solution was filtered into 10 liters of cold water. Very dilute hydrochloric acid was then added until the solution was distinctly acid. A very voluminous, bright red precipitate filled the flask. Under the microscope the material was seen to be in the form of extremely fine, silky hairs. The red product was filtered off, washed, and then shaken with a liter of water, filtered, and washed again. When allowed to stand in water for any length of time, or when allowed to stand while still moist after being filtered, it changed into green pyrogallolsulfonephthalein. It was dried by pressing it between sheets of drying paper. When almost dry, it was crushed and allowed to dry in the air for a week. The analyses show that the substance is *sulfonegallein* with 3 molecules of water of crystallization.

Anal. Subs., 0.5597, 0.4947: loss at 130°, 0.0667, 0.0583. Calcd. for C₁₉H₁₂O₈S + 3H₂O; H₂O, 11.90. Found: H₂O, 11.92, 11.79.

Subs. (dry), 0.4820, 0.4057: BaSO₄, 0.2822, 0.2363. Subs. (dry), 0.1959, 0.1893: CO₂, 0.4085, 0.3959; H₂O, 0.0595, 0.0600. Calcd. for C₁₉H₁₂O₈S: S, 8.01; C, 56.98; H, 3.02. Found: S, 8.04, 8.00; C, 56.87, 57.04; H, 3.40, 3.55.

After loss of the 3 molecules of water at 130°, it did not lose any additional weight when heated to 200°. It does not melt below 315°.

Action of Ammonia Gas.—When exposed to dry ammonia gas until it no longer gained in weight, pyrogallolsulfonephthalein absorbed a little over 4 molecules of ammonia, and turned a bronze-blue.

Anal. Subs., 0.2768, 0.3102: Gain, 0.0483, 0.0558. Calcd. for C₁₉H₁₄O₈S + 4NH₃: NH₃, 14.01. Found: 14.86, 13.25.

When placed in a desiccator over concd. sulfuric acid and allowed to come to constant weight, it then contained one molecule of ammonia.

Anal. Subs., 0.2768, 0.3102: NH_3 , 0.0107, 0.0135. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_9\text{S} + \text{NH}_3$: NH_3 , 3.91. Found: 3.72, 4.17.

Sulfonegallein, dried at 130° , also absorbs between four and five molecules of ammonia, and retains one when kept in a desiccator over concd. sulfuric acid.

The red ammonium salt of pyrogallolsulfonephthalein,⁷ crystallized from water has the composition represented by the formula $\text{C}_{19}\text{H}_{13}\text{O}_9\text{SNH}_4 + 2\text{H}_2\text{O}$. The monosodium salt of pyrogallolsulfonephthalein ($\text{C}_{19}\text{H}_{13}\text{O}_9\text{SNa} + 5\text{H}_2\text{O}$) crystallizes from water in needles with a reddish-brown color and slightly purplish on the surface.

When heated to 200° this salt dried, at 135° , lost another molecule of water (of constitution), leaving the monosodium salt of *sulfonegallein*.

The dizinc salt of pyrogallolsulfonephthalein ($\text{C}_{19}\text{H}_{10}\text{O}_9\text{SZn}_2 + 5\text{H}_2\text{O}$) crystallized from water had a bronze-green surface color and ground to a reddish-purple powder.

Unlike the sodium and ammonium salts of pyrogallolsulfonephthalein, the dizinc salt is only sparingly soluble in water. When heated to 200° , the dried salt loses a molecule of water of constitution, forming the dizinc salt of *sulfonegallein*.

The blue lead salt of pyrogallolsulfonephthalein ($(\text{C}_{19}\text{H}_{11}\text{O}_9\text{S})_2\text{Pb}_3$) does not lose any weight when heated to 200° .

The reaction of pyrogallolsulfonephthalein with a soluble lead salt is very delicate and might be used as a test for either substance.

The barium salt of pyrogallolsulfonephthalein ($(\text{C}_{19}\text{H}_{13}\text{O}_9\text{S})_2\text{Ba} + 6\text{H}_2\text{O}$) from water when dried at 130° does not lose any further weight when heated at 200° .

The normal salts of pyrogallolsulfonephthalein are red and give red solutions, while the salts formed in which some of the hydroxyl groups in the pyrogallol residues are also neutralized are blue and give blue solutions.

Action of Aniline.—When boiled with aniline, pyrogallolsulfonephthalein gives red crystals of an aniline salt of *sulfonegallein*. These lost no weight when heated to 200° and did not melt below 315° .

Anal. Subs. (dry), 0.7192, 0.6599: cc. of 0.1 N H_2SO_4 , 14.78, 13.56. Subs. (dry), 0.5631, 0.5631: BaSO_4 , 0.2612, 0.2590. Calcd. for $\text{C}_{19}\text{H}_{11}\text{O}_9\text{S}(\text{C}_6\text{H}_5\text{NH}_2)$: N, 2.84; S, 6.50. Found: N, 2.88, 2.88; S, 6.37, 6.32.

The reaction is quantitative. The salt is insoluble in almost all of the usual organic solvents, but is slightly soluble in water and in the alcohols.

Sulfonegallein Tetra-acetate.—When 10 g. of dry pyrogallolsulfonephthalein was boiled with 100 cc. of acetic anhydride for three hours, and half the solvent distilled, large, clear, yellow crystals were obtained. By boiling the solution in dry toluene repeatedly with bone black, the tetra-acetate was obtained as colorless, diamond-shaped crystals which melted at 218° with decomposition to a red liquid. The tetra-acetate was allowed to dry in the air for a day and analyzed.

Anal. Subs., 0.2311, 0.1858: loss at 130° , C_7H_8 , 0.0233, 0.0192. Calcd. for $\text{C}_{19}\text{H}_5\text{O}_9\text{S}(\text{C}_2\text{H}_3\text{O})_4 + \text{C}_7\text{H}_8$: toluene, 13.94. Found: 10.08, 10.33.

Subs. (dry), 0.2078, 0.1666: BaSO_4 , 0.0850, 0.0690. Subs. (dry), 0.3348: cc. of 0.1 N NaOH , 23.45. Calcd. for $\text{C}_{19}\text{H}_5\text{O}_9\text{S}(\text{C}_2\text{H}_3\text{O})_4$: S, 5.64; $\text{C}_2\text{H}_3\text{O}$, 30.29. Found: S, 5.62, 5.69; $\text{C}_2\text{H}_3\text{O}$, 30.13.

The tetra-acetate hydrolyzes slowly in the air, more rapidly in water and very readily in alkaline solution.

⁷ The details for the preparation of the salts of pyrogallolsulfonephthalein and the analytical data will be found in the dissertation of Mr. N. Fuchs in the Library of Cornell University.

That the sulfonegallein tetra-acetate contains a pyrone ring is indicated by the color changes when it is slowly saponified with sodium hydroxide solution. It shows first a green fluorescence which rapidly changes to a blue color. The acetyl groups are saponified off and the mono-, di- and tri-acetyl compounds form sodium salts that show the green fluorescence as they contain the pyrone ring. When the saponification is complete, the sulfonegallein is converted into pyrogallolsulfonephthalein by the addition of a molecule of water and hence the blue color in alkaline solution.

As was to be expected, the same tetra-acetate was obtained by boiling sulfonegallein with acetic anhydride.

Sulfonegallein Tetrabenzoate.—Five g. of pyrogallolsulfonephthalein was boiled with 25 g. of benzoyl chloride for two hours and the excess of benzoyl chloride evaporated in a water oven. The brown solid was washed with ether. Three crystallizations from dry benzene gave colorless, transparent needles which melted sharply at 235° to give a reddish liquid. When ground for analysis in an agate mortar, they became strongly electrified. The air-dried sample lost practically no weight when heated at 135°.

Anal. Subs., 0.4873, 0.4383; BaSO₄, 0.1368, 0.1224. Calcd. for C₁₉H₅O₈S-(COC₆H₅)₄: S, 3.93. Found: 3.86, 3.84.

Like the tetra-acetate, the tetrabenzoate of *sulfonegallein* gives a green fluorescence and then a blue color when it is slowly saponified with sodium hydroxide solution, but it is much more stable than the tetra-acetate.

Monomethyl Ether of Pyrogallolsulfonephthalein.—Four g. of *o*-sulfobenzoic acid anhydride and 4 g. of pyrogallol-1-methyl-ether⁸ were heated at 135–145° for six hours. The red mass was boiled with 300 cc. of water; clusters of fine, radiating, red needles crystallized from the solution. These were recrystallized twice from methanol. The crystals had a brick-red color and crumbled to a powder when left in the air. They did not show a definite melting point, but decomposed at about 270°, turning dark green. The product was dried at 125° and analyzed.

Anal. Subs., 0.1971, 0.2054; AgI, 0.1154, 0.1127. Calcd. for C₁₉H₁₃O₈S(OCH₃): CH₃O, 7.18. Found: 7.74, 7.25.

From the method used in preparing this compound, the *dimethyl* ether of pyrogallolsulfonephthalein was to have been expected. But the analyses show, and the purple color in alkaline solution indicates that the substance is the *monomethyl* ether.

Sodium Salt of the Trimethyl Ether of Pyrogallolsulfonephthalein.—Twenty g. of pyrogallolsulfonephthalein was boiled in a liter of absolute methyl alcohol; 50 g. of methyl iodide, and 125 cc. of a solution of sodium methylate (made by adding 9 g. of sodium to 250 cc. of absolute methanol) were added. After the mixture had boiled for an hour, 50 g. of methyl iodide and 125 cc. of sodium methylate solution were again added. The solution turned blue and then red again. After boiling for eight hours, the red solution was concentrated to 100 cc., cooled and added to 1.5 liters of cold, anhydrous ether stirred mechanically. Twenty-one g. of material, brick-red when moist but green on drying, was filtered from the ethereal solution. This product was extracted repeatedly with boiling acetone. Most of it remained undissolved. The acetone solution yielded a few grams of crystals when it was distilled to a small volume. These were recrystallized twice from acetone and were obtained as small red crystals. They were dried at 140° and analyzed.

Anal. Subs., 0.4176; Na₂SO₄, 0.0628. Subs., 0.1346, 0.2444; AgI, 0.1905, 0.3538. Calcd. for C₁₉H₁₀O₈SNa(OCH₃)₃: Na, 4.77; CH₃O, 19.34. Found: Na, 4.87; OCH₃, 18.70, 19.13.

⁸ Graebe and Hess, *Ann.*, **340**, 232 (1905).

The addition of sodium hydroxide solution to an aqueous solution of this sodium salt causes the red color to change to reddish-brown, but no blue color is obtained because the presence of methoxyl groups in place of the hydroxyl groups prevents the formation of a poly sodium salt.

Trimethyl Ether.—The material left undissolved after the acetone extractions, in the experiment described above, was dissolved in a small amount of water and acidified with hydrochloric acid. From the appearance of the crystals that were precipitated, some of which were red and others orange, it seemed probable that there were at least two compounds present. The material was extracted thrice with 200cc. portions of glacial acetic acid. About half of the substance remained undissolved as a yellow powder, from which was obtained the dimethyl ether of *sulfonegallein* (see below). The acetic acid extracts gave purple-red crystals with a small amount of orange crystals. The purple-red crystals were much heavier than the orange ones, so the latter were decanted with the acetic acid from the purple-red ones. These were recrystallized twice from glacial acetic acid and then from methanol, being obtained finally as red crystals with a purplish surface tinge. The air-dried material lost very little weight when heated at 140° and did not melt when heated to 315°.

Anal. Subs. (dry), 0.1918, 0.2068: AgI, 0.2851, 0.3061. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3$: CH_3O , 20.22. Found: 19.64, 19.56.

The trimethyl ether of pyrogallolsulfonephthalein is somewhat soluble in water giving a reddish-orange solution. In dil. sodium hydroxide solution it has a light brown color. It is slightly soluble in ethanol and is insoluble in ether, acetone, benzene and chloroform.

ACTION OF AMMONIA GAS.—When the trimethyl ether was exposed to dry ammonia gas until it no longer gained in weight it absorbed about 3 molecules of ammonia.

Anal. Subs. (dry), 0.2190: gain, 0.0220. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3 + 3NH_3$: NH_3 , 9.99. Found: 9.13.

A mono-ammonium salt remained when this product was allowed to stand in a desiccator over concd. sulfuric acid until it came to constant weight.

Anal. Subs., 0.2190: gain, 0.0070. Calcd. for $C_{19}H_{11}O_6S(OCH_3)_3 + NH_3$: NH_3 , 3.57. Found: 3.10.

The fact that the trimethyl ether absorbs 3 molecules of ammonia is additional proof that it is a derivative of pyrogallolsulfonephthalein and not of *sulfonegallein*.

Dimethyl Ether of Sulfonegallein.—The yellow powder left undissolved after the extraction with boiling acetic acid in the above experiment was recrystallized four times from methanol. When the crystals came out of a concentrated solution they were red and came down to a sharp point at one end, but when obtained from a dilute solution they were golden-orange in color and rectangular in shape. Homogeneous samples of both forms were separated and analyzed. Neither form lost weight when heated at 130° or at 200°, and neither form melted when heated at 315°.

Anal. Subs. (red modification), 0.2588: AgI, 0.2915. Subs., 0.4719: $BaSO_4$, 0.2531. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2$: CH_3O , 14.49; S, 7.49. Found: CH_3O , 14.88; S, 7.37.

These analyses show that the red crystals are the dimethyl ether of *sulfonegallein*.

Subs. (orange modification), 0.2985: AgI, 0.3292. Subs., 0.3033: $BaSO_4$, 0.1616. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2$: CH_3O , 14.49; S, 7.49. Found: CH_3O , 14.57; S, 7.32.

These analyses show that the orange form is also the dimethyl ether of sulfonegallein. The two forms appear to be dimorphous modifications of the same compound. They can be converted one into the other by properly controlling the concentration of the solution. When crystallized from water they both give crystals of the orange form.

Professor Vieweg made the following report on the crystals. "The dimethyl ether has two modifications, the orange and the red. The crystals of either kind were not sufficiently large to allow measurements with the goniometer, but the crystallization could be determined with the microscope. Both varieties crystallize in the *rhombic* system. The orange crystals were rectangular tablets. They are strongly pleochroic. The red crystals have a blue metallic surface color. The pleochroism is similar to that of the orange variety, being greenish-yellow parallel to the elongation, and yellow-orange perpendicular to it. The intensity of color seems to be greater in the red crystals than in the orange, considering those of approximately the same thickness. It is interesting to note that there is a marked similarity between these two forms of the dimethyl ether, and crystals of red and yellow fluorescein, both crystallographically and with reference to the pleochroism."

Both forms have the same solubility and give the same reactions. They dissolve in dil. aqueous sodium hydroxide with development of an orange color and a pink *fluorescence*. Considering the fluorescence to be indicative of the presence of a pyrone ring, we have here further evidence that the dimethyl ethers are derivatives of *sulfonegallein* rather than of pyrogallolsulfonephthalein.

Action of Ammonia Gas on the Dimethyl Ether of Sulfonegallein.—When dry, ground samples of the red form and of the orange form of the dimethyl ether were exposed to dry ammonia gas until they no longer gained in weight; each absorbed 3 molecules of ammonia and turned a little darker in color. In the analyses below, I refers to the red form and II to the orange form.

Anal. Subs. (dry), I, 0.1353; II, 0.1033; gain, I, 0.0166; II, 0.0123. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2 + 3NH_3$: NH_3 , 10.66. Found: I, 10.93; II, 10.64.

On allowing the samples saturated with ammonia to stand in a desiccator over concd. sulfuric acid until they came to constant weight it was found that a mono-ammonium salt was formed in each case.

Anal. Subs., I, 0.1353; II, 0.1033; Gain, I, 0.0053; II, 0.0042. Calcd. for $C_{19}H_{10}O_6S(OCH_3)_2 + NH_3$: NH_3 , 3.83. Found: I, 3.77; II, 3.91.

Dibromo-pyrogallolsulfonephthalein.—To 8.5 g. of pyrogallolsulfonephthalein in 200 cc. of absolute ethanol was added 20 g. of bromine in 100 cc. of absolute ethanol, and the mixture boiled for six hours. The greenish, crystalline product was purified by dissolving it in boiling water and adding hydrochloric acid. The acidified solution gave glistening green crystals when it cooled. They were red when ground.

Anal. Subs., 0.2224, 0.3713; 0.2107; loss at 145° , 0.0222, 0.0371; 0.0253. Calcd. for $C_{19}H_{12}O_9SBr_2 + 4H_2O$: H_2O , 11.12. Found: 9.98, 9.99, 12.01.

Subs. (dry), 0.2002, 0.3342; AgBr, 0.1303, 0.2196. Calcd. for $C_{19}H_{12}O_9SBr_2$: Br, 27.75. Found: 27.70, 27.96.

Dibromo-pyrogallolsulfonephthalein dissolves somewhat in water with development of a purplish-red color and is slightly soluble in the alcohols, but is insoluble in most of the organic solvents. Sodium hydroxide solution dissolves it very readily, producing in very dilute solutions of the alkali a deep red color due to the formation of a monosodium salt, and in an excess of the alkali a deep blue color caused by the formation of a polysodium salt, but the solutions show no fluorescence. It does not melt when heated to 315° .

After being dried at 145° , the dibromo-pyrogallolsulfonephthalein lost another molecule of water (of constitution) when heated to 200° , forming *dibromo-sulfonegallein*.

Anal. Subs. (dry), 0.3113, 0.1672; loss at 200° , 0.0092, 0.0045. Calcd. for $C_{19}H_{12}O_9SBr_2$: loss of $1H_2O$, 3.13. Found: 2.96, 2.69.

ACTION OF AMMONIA GAS.—When dry dibromo-pyrogallolsulfonephthalein was ex-

posed to dry ammonia gas until it no longer gained in weight, it absorbed almost 6 molecules of ammonia, and became dark red.

Anal. Subs. (dry), 0.2976: gain, 0.0498. Calcd. for $C_{19}H_{12}O_9SBr_2 + 6NH_3$: NH_3 , 15.07. Found: 14.33.

On allowing the dibromo-pyrogallolsulfonephthalein saturated with ammonia to stand in a desiccator over concd. sulfuric acid until it came to constant weight, it was found that the substance retained almost 3 molecules of ammonia.

Anal. Subs., 0.2976: gain, 0.0228. Calcd. for $C_{19}H_{12}O_9SBr_2 + 3NH_3$: NH_3 , 8.15. Found: 7.12.

When *dibromo-sulfonegallein* was exposed to dry ammonia gas it absorbed 5 molecules, and retained 3 of them in a desiccator over sulfuric acid.

AMMONIUM SALT.—This salt was made in the same way as the ammonium salt of pyrogallolsulfonephthalein. The needle-shaped crystals were bronze-green by reflected light and were ground to a reddish-brown powder.

Dibromo-sulfonegallein Tetrabenzoate.—Five g. of dry dibromopyrogallolsulfonephthalein was boiled with 35 g. of benzoyl chloride, evaporated in a water-oven and the last traces of benzoyl chloride removed by washing the dark solid remaining with a little ether. The product was purified by boiling it with benzene, using bone black. After three recrystallizations from benzene, it was obtained as colorless, needle-like crystals, which melted to a reddish liquid at 269–270°. The air-dried crystals lost no weight when heated at 120°.

Anal. Subs., 0.3806, 0.2994: AgBr, 0.1459, 0.1135. Calcd. for $C_{19}H_6O_9SBr_2(COC_6H_5)_4$: Br, 16.41. Found: 16.31, 16.13.

Dibromo-sulfonegallein tetrabenzoate is very soluble in benzene and in chloroform, and is only slightly soluble in ether. It is practically insoluble in water, but hydrolyzes slowly in it. It shows a green fluorescence in dil. sodium hydroxide solution, but this soon changes to the blue color that dibromo-pyrogallolsulfonephthalein has in alkaline solution, showing that saponification has taken place.

Pyrogallolsulfonephthalin.—A suspension of 5 g. of pyrogallolsulfonephthalein and 10 g. of zinc dust in 100 cc. of water was boiled for an hour. The mixture first became blue due to the formation of the zinc salt of pyrogallolsulfonephthalein, but this was soon reduced to the zinc salt of pyrogallolsulfonephthalin, leaving the solution with a faint orange-brown color. The excess of zinc dust was filtered off and 400 cc. of concd. hydrochloric acid added. Lustrous, transparent, silvery-brown crystals began to form very rapidly. They were again crystallized by the addition of a large excess of concd. hydrochloric acid. After five such recrystallizations, the crystals were almost colorless. They were dried in a vacuum desiccator over concd. sulfuric acid and ground sodium hydroxide and analyzed.

Anal. Subs., 0.3485, 0.4065: loss at 120°, 0.0159, 0.0149. Calcd. for $C_{19}H_{16}O_9S + H_2O$: H_2O , 4.11. Found: 4.56, 3.67.

Subs. (dry), 0.3326, 0.3916: $BaSO_4$, 0.1844, 0.2169. Calcd. for $C_{19}H_{16}O_9S$: S, 7.63. Found: 7.62, 7.61.

When heated in a melting-point tube, it contracts to a dark red tar at 146–147° but it does not fuse to the glass until the temperature reaches 170°. At about 226° it foams and decomposes. Pyrogallolsulfonephthalin is readily oxidized to pyrogallolsulfonephthalein. It turns red even when kept in a tightly corked vial. It dissolves in dil. sodium hydroxide solution without development of color, but when the solution is allowed to stand in the air, oxidation takes place and the solution turns blue, due to the formation of the polysodium salt of pyrogallolsulfonephthalein. Pyrogallolsulfonephthalin is very soluble in methanol, ethanol, ether, acetone, glacial acetic acid and water but is insoluble in chloroform and carbon tetrachloride.

ZINC SALT.—A suspension of 5 g. of pyrogallolsulfonephthalein and 10 g. of zinc dust in 100 cc. of water was boiled for an hour. The excess of zinc was filtered off and the filtrate concentrated to 25 cc. in the presence of a small piece of zinc. To prevent oxidation of the solution it was cooled in carbon dioxide and stoppered tightly. Crystals with a slight pink tint formed. These, with the zinc that had been added, were filtered off rapidly and the crystals then dissolved in a small volume of hot water. This solution was filtered from the zinc directly into a large test-tube that was then tightly corked and set aside for crystallization to take place. The crystals obtained in this way were colorless except for a slight pink tint. They seemed to lose moisture slowly when left in the air, and crumbled to a powder. Analyses showed the crystals to be the normal zinc salt of pyrogallolsulfonephthalin with 2 molecules of water of crystallization.

Anal. Subs., 0.5021, 0.5847: loss at 125°, 0.0201, 0.0245. Calcd. for $(C_{19}H_{15}O_9S)_2 \cdot Zn + 2H_2O$: H_2O , 3.83. Found: 4.00, 4.19.

Subs. (dry), 0.5188, 0.4975, 0.4820: $ZnSO_4$, 0.0897, 0.0870, 0.0838. Subs. (dry), 0.5602, 0.5265: $BaSO_4$, 0.2784, 0.2603. Calcd. for $(C_{19}H_{15}O_9S)_2 \cdot Zn$: Zn, 7.23; S, 7.09. Found: Zn, 7.00, 7.08, 7.04; S, 6.83, 6.79.

The zinc salt does not oxidize as readily as pyrogallolsulfonephthalin, although it gives the blue zinc salt of pyrogallolsulfonephthalein when air is passed into an aqueous solution of it.

After being dried at 125°, the zinc salt of pyrogallolsulfonephthalin loses 2 molecules of water of constitution when heated at 200°, forming the zinc salt of the *sulfonegallein*.

Anal. Subs. (dried at 125°), 0.4820: loss at 200°, 0.0185. Calcd. for $(C_{19}H_{15}O_9S)_2 \cdot Zn$: loss of $2H_2O$, 3.99. Found: 3.84.

Summary

1. 2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic acid and its tribenzoate have been isolated. 2,3,4-Trihydroxybenzoyl-benzene-*o*-sulfonic acid is an intermediate product in the formation of pyrogallolsulfonephthalein. When heated alone or with pyrogallol, it gives pyrogallolsulfonephthalein.

2. Methods for the preparation of pure, crystallized pyrogallolsulfonephthalein ($C_{19}H_{14}O_9S$) have been given. It is best made from the anhydride of *o*-sulfobenzoic acid and pyrogallol. Pyrogallolsulfonephthalein does not fluoresce in alkaline solution.

3. Sulfonegallein ($C_{19}H_{12}O_8S$) has been made by heating pyrogallolsulfonephthalein at 200°, and by acidifying a dilute alkaline solution of pyrogallolsulfonephthalein *in the cold*. Sulfonegallein reverts to pyrogallolsulfonephthalein in the presence of water. When pyrogallolsulfonephthalein reacts with certain reagents derivatives of sulfonegallein result.

4. Pyrogallolsulfonephthalein, as well as sulfonegallein, reacts as a tautomeric substance, giving *colored* quinoid and *colorless* lactoid derivatives. Pyrogallolsulfonephthalein and its salts, and sulfonegallein and its salts are colored compounds having the quinoid structure. The colorless tetra-acetate and tetrabenzoate of *sulfonegallein* are derivatives of the lactoid form.

5. The *colored* monomethyl and trimethyl ethers of pyrogallolsulfonephthalein and the dimethyl ether of *sulfonegallein*, as well as their colored ammonium salts, have been made and have the quinoid structure.

6. Dibromo-pyrogallolsulfonephthalein is a tautomeric substance, having for itself and its ammonium salt the colored quinoid structure, and forming the colorless, dibromo-*sulfonegallein* tetrabenzoate, which has the lactoid structure.

7. Pyrogallolsulfonephthalin and its zinc salt have been made. They are colorless. Pyrogallolsulfonephthalin is very readily oxidized by the air to pyrogallolsulfonephthalein.

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RING CLOSURE IN CHLORO-ALKYL PHENYL CARBAZATES. SIX- AND SEVEN-MEMBERED HYDRAZOLACTONES

By ARTHUR W. DOX

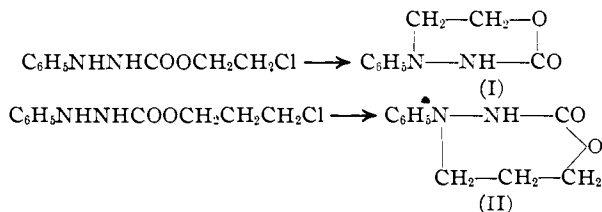
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The tendency of cyclic compounds to form when halogen and hydrogen are removed by simple treatment with alkali from the terminal atoms of a five- or six-membered open chain has made possible the synthesis of numerous new heterocyclic structures. In a previous paper¹ this reaction was applied to the synthesis of 1,3-oxazine derivatives from γ -chloropropyl carbanilates. It was shown that such ring closure took place only when the amide grouping was stabilized by the introduction of phenyl; otherwise, a decomposition occurred with formation of alkali cyanate.

A similar reaction should occur with chloro-alkyl phenylcarbazates, which are analogous to the carbanilates except for the presence of an additional NH group, and the ring closure should yield cyclic derivatives with two nitrogens and one oxygen as the hetero elements.

The two esters studied were the β -chloro-ethyl and the γ -chloropropyl. Assuming that the terminal NH of the phenylcarbazic acid group furnishes the hydrogen which is split out as hydrogen chloride, the resulting cyclic derivatives should contain six and seven members, respectively.



Such heterocycles containing an oxygen in the ring adjacent to a carbonyl may also be regarded as lactones and should be hydrolyzed easily by aqueous alkali. Hence, the yield is better when sodium ethoxide in absolute

¹ Dox and Yoder, THIS JOURNAL, 45, 723 (1923).