

Anal. Subs., 0.2103, 0.2206: CO₂, 0.5338, 0.5578; H₂O, 0.1498, 0.1580. Calcd. for C₁₆H₂₂O₄: C, 69.02; H, 7.97. Found: C, 69.23, 68.96; H, 7.92, 7.96.

Coumarin.—In 13 g. of aceto-acetic ester was dissolved 19.4 g. of hexylresorcinol, and solution was slowly added to 400 g. of cold, 82% sulfuric acid. The mixture was left for 24 hours and then poured onto ice. The sticky substance that separated gradually solidified. It was washed several times with water and was crystallized from alcohol. Ten g. of pure substance was obtained; m. p., 165°; yield, 39%.

Anal. Subs., 0.1207, 0.1116: CO₂, 0.3254, 0.3014; H₂O, 0.0836, 0.0773. Calcd. for C₁₆H₂₀O₃: C, 73.85; H, 7.75. Found: C, 73.53, 73.65; H, 7.70, 7.60.

My thanks are due to Mr. L. C. Copeland for his assistance with several of the preparations.

Summary

1. Caproylresorcinol was prepared by the condensation of ethyl caproate with resorcinol.
2. A comparative study was made of the behavior of caproylresorcinol and of hexylresorcinol with regard to methylation, reaction with acid chlorides, nitration, bromination and formation of coumarin.

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META-CRESOLSULFONEPHTHALEIN, 3,6-DIMETHYLSULFONEFLUORAN AND SOME OF THEIR DERIVATIVES

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The condensation of *m*-cresol with the anhydride or chlorides of *o*-sulfobenzoic acid was undertaken to prepare *m*-cresolsulfonephthalein. No mention of this phthalein was found in the literature. While this work was in progress, however, Cohen² published a preliminary note in which he mentioned *m*-cresolsulfonephthalein and tetrabromo-*m*-cresolsulfonephthalein. He stated that the former gave a color change from yellow to purple at a *P*_H of 7.6–9.2, while the latter changed from yellow to blue-green at a *P*_H of 4.0–5.6, but he gave no details as to the method of preparation or properties of these sulfonephthaleins, nor were any analyses given.

Investigations carried out in this Laboratory³ have shown that the con-

¹ From a dissertation presented by A. C. Purdy to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

We are indebted to the Monsanto Chemical Works, who very kindly furnished gratis the saccharin used in this investigation.

² Cohen, "Some New Sulfonephthalein Indicators," *Pub. Health Repts.*, **38**, 199 (1923).

³ Orndorff and Sherwood, *THIS JOURNAL*, **45**, 486 (1923). Orndorff and Vose, *ibid.*, **46**, 1896 (1924). Orndorff and Cornwell, *ibid.*, **48**, 981 (1926).

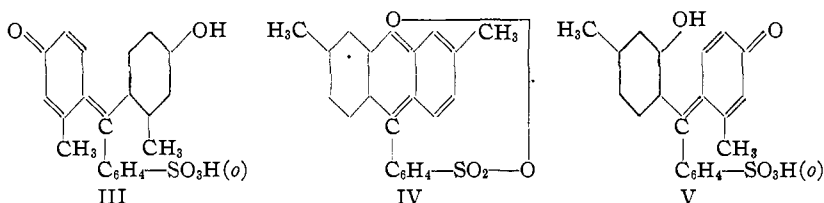
condensation of a phenol with the anhydride of *o*-sulfobenzoic acid takes place in two stages, an addition product, the intermediate acid being first formed, which then reacts with a second molecule of the phenol to give the sulfonephthalein. In the case of *m*-cresol there are two such intermediate acids (I and II) theoretically possible.



I. 2'-Hydroxy-4'-methyl-benzoyl-benzene-2-sulfonic acid.

II. 4'-Hydroxy-2'-methyl-benzoyl-benzene-2-sulfonic acid.

These intermediate acids on condensation with *m*-cresol could form three possible compounds (III, IV and V).



m-Cresolsulfonephthalein (III), the di-*para* compound in which the hydroxyl groups are *para* to the methane carbon atom, was isolated from the condensations carried on at a temperature of 105–110°. Dimethylsulfonefluoran (IV), the anhydride of the di-*ortho* compound, was obtained from the condensation carried on above 135°. The *ortho-para* compound (V) was not obtained. *m*-Cresolsulfonephthalein (III) was shown to be the di-*para* compound by fusing it with solid sodium hydroxide and isolating 5-hydroxyl-1-methyl-2-benzoic acid from the products of the decomposition. In a like manner the dimethylsulfonefluoran (IV) was shown to be the anhydride of the di-*ortho* compound by identifying 3-hydroxy-1-methyl-4-benzoic acid among the products of its decomposition with alkali.

m-Cresolsulfonephthalein is a highly colored substance, indicating a quinoid structure. Since the crystalline material always contains about 1% of water, it may be considered a solid solution of the inner carbonium or inner oxonium salt and the quinoid hydrate similar to the other sulfonephthaleins³ studied in this Laboratory. *m*-Cresolsulfonephthalein reacts as a tautomeric substance, and colorless derivatives of the lactoid form and colored derivatives of the quinoid form were made. A colorless modification of *m*-cresolsulfonephthalein was not obtained.

The red *m*-cresolsulfonephthalein dissolves in water with development of a yellow color, due to the formation of the carbinol and a small amount of the quinoid hydrate. When this solution is heated it assumes an orange-red color, as some of the carbinol is converted into the quinoid

hydrate, which loses water to give the quinoid form of the phthalein. Strong acids also give a red color when added to the *yellow* solution of the phthalein, due to the conversion of some of the carbinol into the quinoid hydrate, which then splits off water to form the quinoid salt with the acid.⁴ Alkaline solutions of this sulfonephthalein are purple, due to the formation of highly colored salts with a quinoid structure.

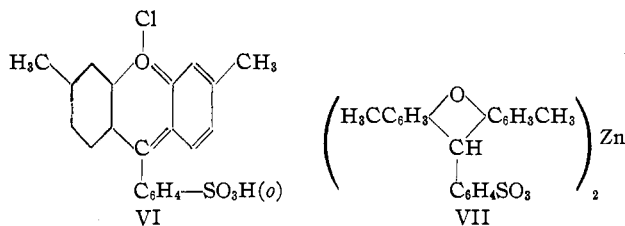
Tetrabromo-*m*-cresolsulfonephthalein was obtained in the *colorless*, lactoid form, but it gives a colored hydrate having the quinoid structure. On being heated, however, this hydrate loses water and leaves the colorless, tetrabromo compound.

Unlike the fluorans previously investigated, 3,6-dimethylsulfonefluoran (IV) is a colored compound. Its color and its neutral character point to its being an inner oxonium or carbonium salt.

This sulfonefluoran does not absorb ammonia but it combines with one molecule of dry hydrogen chloride, giving a colored hydrochloride (VI) with an *ortho*-quinoid structure.

When this substance is dissolved in concd. sulfuric acid the solution exhibits the fluorescence characteristic of fluorans.

When suspended in water, dimethylsulfonefluoran is reduced by boiling with zinc dust, giving the zinc salt of dimethylhydrosulfofluoranic acid (VII).



This is a very stable salt, showing that its structure no longer resembles that of the sulfonefluoran, which does not form salts.

On bromination of the sulfonefluoran, a dibromodimethylsulfonefluoran was obtained. This also is a highly colored product. The introduction of the bromine atoms increases the acid properties of the sulfonefluoran as the dibromo derivative absorbs ammonia and gives a stable tri-ammonia compound. Because of its color the dibromo compound is also to be represented as an inner oxonium or carbonium salt. The position of the bromine atoms in the molecule was not determined.

Experimental Part

m-Cresol.—The *m*-cresol used was obtained from Kahlbaum and from Eastman. The first sample boiled at 199.3–200.3° (742.3 mm.) and gave a freezing point of 4.75°. The second (*m*-cresol, “practical”) boiled at

⁴ See benzaurin, *THIS JOURNAL*, 47, 2770 (1925).

199.0–199.8° (737.5 mm.). A quantitative determination of the *m*-cresol in these products by the Barrett modification of the Raschig nitration method gave 90.8% for the former and 98.2% for the latter. The impurity is presumed to be *p*-cresol. Dawson and Mountford's⁵ freezing-point curve for mixtures of *m*- and *p*-cresol gave 91.36% of *m*-cresol in the mixture freezing at 4.75°.

Condensation of *m*-Cresol with *o*-Sulfobenzoic Acid Anhydride.—The products of the condensation of *m*-cresol with *o*-sulfobenzoic acid anhydride depend on the temperature.

A. Condensations below 110°.—The anhydride⁶ (1 mole) was dissolved in *m*-cresol (2 moles plus a slight excess), and zinc chloride (weight equal to that of the *m*-cresol) was slowly added during stirring. This mixture was heated at 105–108° until the mass solidified. Water was then added and the excess of *m*-cresol removed by steam distillation. The residue was extracted with a hot 10% sodium carbonate solution, the extract filtered, diluted and acidified with dil. hydrochloric acid. On cooling, the sulfonephthalein was obtained as fine, beetle-green crystals. The zinc chloride did not increase the yield but shortened the time necessary for the reaction. Yields of the sulfonephthalein were about 15%.

B. Condensation from 125–145°.—A mixture of *m*-cresol and the anhydride in the proportions given above was heated for 48 hours at 145°, but no condensing agent was employed. The mixture was then thoroughly extracted with hot water. The water solutions were concentrated to crystallization, and the yellow-orange crystalline product was recrystallized from hot water. On analysis this product, which was obtained with a 20% yield, proved to be dimethylsulfonefluoran (IV).

Product Insoluble in 10% Sodium Carbonate.—In all the fusions of *m*-cresol with the anhydride of *o*-sulfobenzoic acid very appreciable quantities of a highly colored substance insoluble in water and 10% sodium carbonate solution were obtained. It contained about 3–4% of sulfur, but the results of the analyses varied and all attempts to prepare the substance itself or any of its derivatives in a pure crystalline condition were unsuccessful.

Reaction of *m*-Cresol with the Chlorides of *o*-Sulfobenzoic Acid.—A modification of the method of Remsen and Dohme⁷ was used to prepare the chlorides. *m*-Cresol was condensed with the sulfonechlorides, at a temperature of 105–110°, using zinc chloride as a condensing agent. The proportions used and the treatment of the reaction product were the same as described above in the anhydride condensations below 110°. Yields of 20% of the pure *m*-cresolsulfonephthalein were obtained by this method.

⁵ Dawson and Mountford, *J. Chem. Soc.*, **113**, 923 (1918).

⁶ White and Acree, *THIS JOURNAL*, **41**, 1197 (1919).

⁷ Orndorff and Cornwell, *ibid.*, **48**, 981 (1926).

***m*-Cresolsulfonephthalein.**—Air-dried samples of the sulfonephthalein were found to contain about 1% of water.

*Anal.*⁸ Subs., 1.1065, 1.0336: loss at 125°, 0.0110, 0.0103. Found: H₂O, 0.99%, 1.0%.

Subs. (dry), 0.3009, 0.3205, 0.3121, 0.3693: BaSO₄, 0.1804, 0.1942, 0.1871, 0.2229. Calcd. for C₂₁H₁₈SO₅: S, 8.38. Found: 8.24, 8.32, 8.23, 8.29. (The first two samples analyzed are from the anhydride condensation and the latter two from the chloride condensation.)

Pure *m*-cresolsulfonephthalein crystallizes with a beetle-green surface color. When ground it gives a deep red powder. From cold alkaline solutions it is precipitated in reddish flocks upon the addition of acid. At the boiling temperature the acid precipitates it in a dark colored, amorphous form. In order to precipitate it in a crystalline form it was found advantageous to acidify a hot 5% sodium carbonate solution of such a dilution that the sulfonephthalein comes out gradually on concentration of the slightly acid solution. *m*-Cresolsulfonephthalein is slightly soluble in water, quite soluble in ethanol and methanol, and acetic acid, and insoluble in benzene, ether, chloroform, carbon tetrachloride, ethyl acetate and petroleum ether. Its saturated aqueous solution is orange-red, changing to bright red on the addition of a mineral or strong organic acid. It dissolves in concd. sulfuric acid with development of a deep cherry-red color. *m*-Cresolsulfonephthalein dissolves in solutions of sodium hydroxide, sodium carbonate and bicarbonate, and ammonium hydroxide, giving a highly colored solution which appears purple in thin layers and red in thick layers. On dilution a purple solution is obtained.

With aniline, *m*-cresolsulfonephthalein reacts in the same way as the other sulfonephthaleins.³ It dissolves with development of a red color, which changes to green when the solution is heated to the boiling point. On cooling and acidifying this solution with hydrochloric acid, a flocculent green precipitate is formed, analogous to the diphenylamine-sulfonephthalein isolated by Sherwood.³ *m*-Cresolsulfonephthalein is practically insoluble in cold dimethylaniline, but dissolves to a slight extent when heated, giving an amber-colored solution.

m-Cresolsulfonephthalein does not have a definite melting point, but deepens in color when heated and gradually shrivels and carbonizes between 250° and 300°.

The following derivatives of *m*-cresolsulfonephthalein were made.

AMMONIUM SALT.—A sample of pure, dry *m*-cresolsulfonephthalein absorbed about 3 molecular proportions of dry ammonia gas. The resulting product was deep red and was easily soluble in water with development of a deep red color. It lost ammonia on standing in a desiccator over concd. sulfuric acid and gave a stable, lighter red monoammonium salt.

⁸ International atomic weights for 1925 were used in the calculations in this paper, THIS JOURNAL, 47, 600 (1925).

Anal. Subs., 0.2245: gain, 0.0096. Calcd. for $C_{21}H_{18}SO_5 + 1 NH_3$: NH_3 , 4.26. Found: 4.10.

BARIUM SALT.—An excess of barium carbonate was boiled with an aqueous suspension of *m*-cresolsulfonephthalein, until the latter had completely dissolved. The filtered solution was evaporated to dryness, and the resulting dark red product was extracted with ethanol. The salt did not crystallize so the alcoholic extract was evaporated to dryness and the residue ground, dried in the air and analyzed. It proved to be the barium salt of *m*-cresolsulfonephthalein containing two molecules of alcohol, which it lost on drying at 135° .

Anal. Subs., 0.2499, 0.2272: loss at 135° , 0.0238, 0.0214. Calcd. for $C_{42}H_{34}S_2O_{10}Ba + 2 C_2H_5OH$: C_2H_5OH , 9.28. Found: 9.52, 9.42.

Subs. (after heating at 135°), 0.4323, 0.4547: $BaSO_4$, 0.1112, 0.1166. Calcd. for $C_{42}H_{34}S_2O_{10}Ba$: Ba, 15.27. Found: 15.14, 15.10.

DIACETATE.—Four g. of pure *m*-cresolsulfonephthalein was boiled with 50 cc. of acetic anhydride for one- and one-half hours. The diacetate was recrystallized from ether, and obtained as colorless needles melting at $172-173^\circ$.

Anal. Subs., 0.3942, 0.3514: $BaSO_4$, 0.1918, 0.1728. Calcd. for $C_{21}H_{16}SO_5-(OCC_2H_5)_2$: S, 6.87. Found: 6.68, 6.75.

The diacetate is readily saponified by cold sodium hydroxide solution, but is not hydrolyzed by boiling water. It is readily soluble in glacial acetic acid and benzene, quite soluble in ether, but insoluble in water and petroleum ether.

DIBENZOATE.—Five g. of pure *m*-cresolsulfonephthalein in 20 g. of benzoyl chloride was heated at $140-145^\circ$ for two hours. The excess of benzoyl chloride was evaporated in a water-oven through which a current of dry air passed. The residue was recrystallized from ether, giving colorless needles; m. p., $208-209^\circ$.

Anal. Subs., 0.3784, 0.3933: $BaSO_4$, 0.1441, 0.1518. Calcd. for $C_{21}H_{16}SO_5-(OCC_6H_5)_2$: S, 5.42. Found: 5.22, 5.30.

The dibenzoate is soluble in benzene, very slightly soluble in cold ether, and insoluble in petroleum ether and water. It is very stable toward cold sodium hydroxide solution, but is slowly saponified by boiling with this solution.

DIMETHYL ETHERS. *A. Colorless Form.*—Ten g. of pure, dry *m*-cresolsulfonephthalein was boiled with 500 cc. of methyl alcohol for 50 hours. The solution was then evaporated to dryness and the residue extracted with ether. The dimethyl ether was obtained as colorless crystals, which turned faintly pink when air-dried. It turns red when heated and melts to a dark red liquid at $164-165^\circ$.

Anal. Subs., 0.2969, 0.3013: $BaSO_4$, 0.1669, 0.1684. Subs., 0.1692, 0.1728: AgI, 0.1989, 0.2018. Calcd. for $C_{21}H_{16}SO_3(CH_3O)_2$: S, 7.81; OCH_3 , 15.13. Found: S, 7.72, 7.66; OCH_3 , 15.53, 15.43.

The colorless dimethyl ether of *m*-cresolsulfonephthalein is very soluble in methyl alcohol, forming a bright red solution, and in benzene, quite soluble in ether and ethanol and sparingly soluble in water. It is very soluble in acetone, without development of color, but the solution becomes red on the addition of a drop of water. It is readily hydrolyzed by boiling with dilute acids; in fact, boiling with water slowly brings about hydrolysis. It is, however, quite stable toward solutions of the alkalies. It is not acetylated by boiling with acetic anhydride, nor does it absorb dry ammonia gas.

The highly colored mother liquor from the crystallization of the colorless dimethyl ether was evaporated to dryness and the residue extracted with benzene. A few dark red crystals were obtained which proved to be a monomethyl ether, melting at $176-178^\circ$.

Anal. Subs., 0.1173: AgI, 0.0674. Calcd. for $C_{21}H_{17}SO_4(CH_3O)$: OCH_3 , 7.83. Found: 7.59.

The fact that it dissolves in dil. ammonium hydroxide and is precipitated by hydrochloric acid without changing its melting point indicates that it is the monomethyl ether rather than the monomethyl ester.

B. Colored Form.—A sample of the pure, dry, colorless dimethyl ether of *m*-cresolsulfonephthalein (in a platinum boat) was heated at 170–172° for 20 minutes in a current of dry carbon dioxide. The dark red liquid solidified on cooling. This solid was ground and exposed to dry ammonia gas. The ether did not change in weight during the heating but gained weight on exposure to the ammonia gas. When placed in a desiccator over sulfuric acid this product formed a stable mono-ammonium salt of the colored dimethyl ether of *m*-cresolsulfonephthalein.

Anal. Subs., 0.2980: gain, 0.0119. Calcd. for $C_{21}H_{16}SO_3(OCH_3)_2 + NH_3$: NH_3 , 3.98. Found: 3.84.

Tetrabromo-*m*-cresolsulfonephthalein.—A solution of 15 g. of bromine in 125 cc. of glacial acetic acid was added to 20 g. of pure *m*-cresolsulfonephthalein in 250 cc. of glacial acetic acid. The mixture was stirred mechanically for 24 hours. The precipitate was then filtered off and extracted with benzene. The tetrabromo compound was crystallized from benzene and recrystallized from glacial acetic acid. Colorless crystals melting at 218–219° were obtained.

Anal. Subs., 0.4837, 0.4720: $BaSO_4$, 0.1551, 0.1547. Subs., 0.1315, 0.1504: $AgBr$, 0.1421, 0.1612. Calcd. for $C_{21}H_{14}Br_4SO_3$: S, 4.59; Br, 45.80. Found: S, 4.41, 4.50; Br, 45.99, 45.60.

Tetrabromo-*m*-cresolsulfonephthalein is readily soluble in ethyl acetate, ether and ethanol, fairly soluble in benzene, somewhat soluble in glacial acetic acid and sparingly soluble in water. It is very sensitive to alkalies, tap water being sufficiently alkaline to give the characteristic blue-green color.

HYDRATE.—The brick red, amorphous hydrate of tetrabromo-*m*-cresolsulfonephthalein was precipitated by the acidification of the aqueous solution of the tetrabromo compound. The hydrate was filtered off, air-dried and a portion of it heated in a melting-point tube. It turned from red to orange at about 90°, became colorless at about 190°, and melted sharply at 218–219°.

Anal. Subs., 0.4730, 0.4997: loss at 130–135°, 0.0725, 0.0765. Calcd. for $C_{21}H_{14}Br_4SO_3 + 7 H_2O$: H_2O , 15.30. Found: 15.33, 15.31.

The hydrate also loses seven molecules of water when allowed to stand in a desiccator over concd. sulfuric acid, but regains this water when placed in a desiccator over water. The substance dried at 130–135° does not gain appreciably in weight when placed in a desiccator over water.

DIACETATE.—The diacetate of the tetrabromo compound was prepared in the same manner as the diacetate of the *m*-cresolsulfonephthalein. It was obtained as colorless needles, melting at 235–236°, by recrystallization from ethyl acetate.

Anal. Subs., 0.5060, 0.5138: $BaSO_4$, 0.1478, 0.1487. Subs., 0.1556, 0.1593: $AgBr$, 0.1486, 0.1518. Calcd. for $C_{21}H_{12}Br_4SO_3(OCCH_3)_2$: S, 4.10; Br, 40.88. Found: S, 4.01, 3.98; Br, 40.64, 40.55.

The diacetate is quite soluble in benzene, ethyl acetate and glacial acetic acid, sparingly soluble in ether and insoluble in water. It is slowly saponified by cold sodium hydroxide solution; more readily by hot alkali. It is readily saponified by cold alcoholic sodium hydroxide solution, but is stable toward boiling water.

DIBENZOATE.—The dibenzoate of the tetrabromo compound was prepared in the same manner as the dibenzoate of the *m*-cresolsulfonephthalein. It was recrystallized from ether, giving colorless crystals melting at 205–206°.

Anal. Subs., 0.5326, 0.5257: $BaSO_4$, 0.1340, 0.1342. Subs., 0.1440, 0.1567:

AgBr, 0.1181, 0.1291. Calcd. for $C_{21}H_{12}Br_4SO_8(OCC_6H_5)_2$: S, 3.54; Br, 35.28. Found: S, 3.46, 3.50; Br, 34.90, 35.06.

The dibenzoate is readily soluble in benzene and ethyl acetate, quite soluble in ether and ethyl alcohol and insoluble in water. It is unaffected by cold aqueous sodium hydroxide, but is slowly saponified by hot alkali. It is readily saponified by hot alcoholic alkali, but it is not decomposed by boiling water.

AMMONIUM SALT.—A sample of pure tetrabromo-*m*-cresolsulfonephthalein absorbed about four molecular proportions of dry ammonia gas. The resulting product was deep purple with a bronze surface color. When allowed to stand in a desiccator over sulfuric acid this compound lost ammonia and yielded a dark colored, stable ammonium salt.

Anal. Subs., 0.4274: gain, 0.0135. Calcd. for $C_{21}H_{14}Br_4SO_8 + 1 NH_3$: NH_3 , 2.38. Calcd. for $C_{21}H_{14}Br_4SO_8 + 2 NH_3$: NH_3 , 4.64. Found: 3.06.

3,6-Dimethylsulfonefluoran (IV)

Analyses of the yellow-orange crystalline product obtained from the condensation of *m*-cresol with the anhydride of *o*-sulfobenzoic acid at 125–145°, show it to be a dimethylsulfonefluoran.

Anal. Subs., 0.3761, 0.4228: $BaSO_4$, 0.2363, 0.2686. Subs., 0.1184, 0.1423, 0.1410: CO_2 , 0.2990, 0.3600, 0.3586; H_2O , 0.0470, 0.0560, 0.0568. Calcd. for $C_{21}H_{16}SO_4$: C, 69.21; H, 4.43; S, 8.80. Found: C, 68.90, 69.02, 69.38; H, 4.44, 4.41, 4.51; S, 8.63, 8.72.

The sulfonefluoran crystallized in flat, orange-colored plates from water or 50% methanol. It was also obtained in small, yellow-orange needles from water. When ground it gives an orange-yellow powder. It does not possess a definite melting point but chars when heated to 280–290°.

Dimethylsulfonefluoran is slightly soluble in water, readily soluble in methanol and chloroform, difficultly soluble in ethanol and acetone, and insoluble in benzene, ether, ethyl acetate and carbon tetrachloride. Its saturated water solution is amber-colored, and undergoes no change in color when heated or acidified. Conc'd. hydrochloric acid precipitates the sulfonefluoran from its aqueous solution in red flocks.

Dimethylsulfonefluoran dissolves in cold conc'd. sulfuric acid with development of an amber color, the solution possessing the characteristic greenish fluorescence of the fluorans. On heating, the solution becomes reddish.

The sulfonefluoran is insoluble in 10% sodium carbonate solution, although the solid particles become greenish. When the solution is filtered and hydrochloric acid is added to the filtrate no precipitate is formed. The sulfonefluoran is soluble, however, in cold 5% sodium hydroxide solution with an intense blue color. Hydrochloric acid precipitates it from this solution in orange-colored flocks.

When heated with aniline, the dimethylsulfonefluoran dissolves with a red color, but the resulting solution does not undergo any change in color on boiling. Boiling with acetic anhydride failed to acetylate it and boiling with zinc or barium carbonate in an attempt to form salts apparently caused decomposition. A sample of the pure dry 3,6-dimethylsulfonefluoran turned greenish when exposed to dry ammonia gas but did not gain appreciably in weight.

HYDROCHLORIDE.—When a sample of pure, dry 3,6-dimethylsulfonefluoran was exposed to the action of dry hydrogen chloride, it rapidly gained in weight and turned a reddish color.

Anal. Subs., 0.2600: gain, 0.0254. Calcd. for $C_{21}H_{16}SO_4 + 1 HCl$: HCl, 9.10. Found: 8.90.

ZINC SALT OF THE REDUCTION PRODUCT OF DIMETHYLSULFONEFLUORAN.—An

aqueous suspension of 5 g. of the sulfonefluoran was boiled with an excess of zinc dust. The sulfonefluoran dissolved with development of a reddish color, but the solution became colorless on continued boiling. When the liquid was filtered, concentrated and cooled, fine colorless needles separated. These were filtered off and dried in a vacuum desiccator. A portion of this product was dried to constant weight at 130–135° in a current of dry carbon dioxide and analyzed.

Anal. Subs., 0.1724, 0.1547: CO₂, 0.4006, 0.3614; H₂O, 0.0666, 0.0629. Subs., 0.3120, 0.4014: ZnSO₄, 0.0623, 0.0797. Calcd. for C₄₂H₃₄S₂O₃Zn: C, 63.35; H, 4.31; Zn, 8.21. Found: C, 63.40, 63.73; H, 4.22, 4.55; Zn, 8.01, 7.97.

The zinc salt of dimethylhydrosulfofluoranic acid is quite soluble in hot water, but difficultly soluble in cold water. It is also quite soluble in ethanol. It is not oxidized when oxygen is passed into a boiling alcoholic solution for several hours, nor is the dry salt oxidized when heated in a water-oven. It is, however, very sensitive to light and turned a deep yellow immediately in direct sunlight. The zinc salt is very stable, and its slight solubility in cold water made it impossible to precipitate the zinc completely as zinc sulfide, nor can the zinc be removed by dilute mineral acids in the cold. When it was heated on a water-bath with dil. sulfuric acid in a stream of carbon dioxide, the resulting product gave no test for zinc and when crystallized from 50% methanol gave dimethylsulfonefluoran.

Dibromo-3,6-dimethylsulfonefluoran.—Four g. of bromine in 25 cc. of glacial acetic acid was slowly added to a solution of 4 g. of pure, dry dimethylsulfonefluoran in 75 cc. of glacial acetic acid during mechanical stirring. After stirring had been continued for 24 hours the crystalline bromine compound was filtered off and air-dried. The air-dried product was orange-red and when ground gave an orange powder. An air-dried sample was dried to constant weight at 125°.

Anal. Subs., 0.2049, 0.2273: loss at 125°, 0.0298, 0.0326. Calcd. for C₂₁H₁₄Br₂SO₄ + 1.5 C₂H₄O₂: C₂H₄O₂, 14.71. Found: 14.54, 14.34.

Another portion of the bromine compound after heating at 125° was analyzed and shown to be dibromo-3,6-dimethylsulfonefluoran.

Anal. Subs., 0.2221, 0.2626: BaSO₄, 0.1022, 0.1197. Subs., 0.1983, 0.3065: AgBr, 0.1415, 0.2183. Calcd. for C₂₁H₁₄Br₂SO₄: S, 6.14; Br, 30.61. Found: S, 6.32, 6.26; Br, 30.37, 30.31.

The dibromo compound is soluble in hot glacial acetic acid, ethanol or methanol and water, slightly soluble in chloroform and insoluble in benzene. When heated it turns dark at about 200°, but does not melt below 300°. In cold, concd. sulfuric acid it gives a yellow solution having a slight, greenish fluorescence.

An attempt to make the tetrabromo compound by bromination in hot glacial acetic acid resulted in dark colored products of varying bromine content, due probably to some of the bromine entering the side chain. There was no evidence of the formation of the oxonium tribromo compound during the bromination in cold glacial acetic acid.

AMMONIUM SALT.—The substitution of two atoms of bromine increases its acid properties so that dibromodimethyl-sulfonefluoran readily absorbs ammonia when placed in dry ammonia gas. When allowed to stand in a desiccator over sulfuric acid this product lost ammonia and yielded a highly colored, stable ammonia compound.

Anal. Subs., 0.1751: gain, 0.0168. Calcd. for C₂₁H₁₄Br₂SO₄ + 3 NH₃: NH₃, 8.66. Found: 8.75.

Summary

1. Pure *m*-cresolsulfonephthalein has been prepared by the condensation of *m*-cresol with the anhydride or chlorides of *o*-sulfobenzoic acid at

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.

ITHACA, NEW YORK

[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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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 Barrett² by condensing *o*-hydroxybenzoyl-*o*-benzoic acid with phenol, and Orndorff and Parsons³ have made isophenol-tetrachlorophthalein from *o*-hydroxybenzoyl-tetra-

¹ 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.

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

³ Orndorff and Parsons, *ibid.*, **48**, 283 (1926).