

removed and the residue fractionated. There was obtained 3 g. of methyl heptenone oxide, b. p. 145–155°; yield, 60%.

0.9651 g. of the ketone was heated under the same conditions and the residue weighed. The brown resinous product amounted to 0.0704 g., equivalent to 7.29%.

Additional experiments in which quantities of 1 to 2 g. of the ketone were heated with small amounts of concentrated sulfuric acid (0.02 to 0.08 g.) under the same conditions, gave results similar to those under the influence of heat alone. There is, therefore, no pronounced tendency for dehydration and polymerization to a resinous product as in the case of methyl γ,δ -dihydroxy amyl ketone.

Summary

1. Attention is drawn to the important role, in the case of dihydroxy-carbonyl derivatives, played by the hydroxyl groups in the γ,δ -positions to the carbonyl group.

2. It is found that methyl γ,δ -dihydroxy amyl ketone behaves similarly to methyl γ,δ -dihydroxy butyl ketone in that it readily undergoes dehydration and polymerization in the presence of a trace of concentrated sulfuric acid. The change corresponds to a loss of one molecule of water from each molecule of the dihydroxy ketone.

3. Under the same conditions methyl γ,δ -dihydroxy *isovaleryl* ketone readily undergoes dehydration with formation of methyl heptenone oxide and shows little tendency towards polymerization. The introduction of the second methyl group in the δ -position thus facilitates to a pronounced degree the splitting off of water from the two adjacent hydroxyl groups.

4. The bearing of such changes on the formation of polysaccharides such as cellulose is indicated.

MONTREAL, CANADA

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

2,7-DIMETHYLSULFONEFLUORAN, 2'-HYDROXY-5'-METHYLBENZOYL-2-BENZENESULFONIC ACID AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND I. T. BEACH¹

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Fluoran was discovered by Baeyer² and its constitution established by Meyer.³ 2,7-Dimethylfluoran was first made by Drewson.⁴ Sulfone-phthaleins have been prepared by Remsen and his students⁵ and also

¹ From a dissertation presented by I. T. Beach to the Faculty of the Graduate School, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Baeyer, *Ann.*, **212**, 347 (1882).

³ Meyer, *Ber.*, **24**, 1412, 3586 (1891).

⁴ Drewson, *Ann.*, **212**, 340 (1882).

⁵ Remsen and co-workers, *Am. Chem. J.*, **6**, 180 (1884); **9**, 372 (1887); **11**, 73 (1889); **16**, 513, 328 (1894); **17**, 352, 656 (1895); **20**, 257 (1898).

in this Laboratory.⁶ The only sulfonefluoran hitherto described appears to be the 3,6-dimethylsulfonefluoran prepared by Orndorff and Purdy.⁷

Since the reactions of the anhydride and the chlorides of *o*-sulfobenzoic acid with *o*-cresol and with *m*-cresol have been investigated, it seemed of interest to study the analogous reactions with *p*-cresol. The present investigation was undertaken for this purpose.

Experimental Part

The *p*-cresol used in this investigation was purified by redistillation. The redistilled material contained less than 0.01% of *m*-cresol. The saccharin was presented by the Monsanto Chemical Works. The acid ammonium salt of *o*-sulfobenzoic acid was prepared by the hydrolysis of saccharin, as described by Blackshear.⁸ The anhydride of *o*-sulfobenzoic acid was made by the interaction of the acid ammonium salt of *o*-sulfobenzoic acid with thionyl chloride.⁹

Condensation of *o*-Sulfobenzoic Anhydride with *p*-Cresol; 2,7-Dimethylsulfonefluoran.—Mixtures of one molecular equivalent of *o*-sulfobenzoic anhydride with slightly more than two molecular equivalents of *p*-cresol were heated in a thermostatically controlled electric oven. No reaction occurred in the absence of a condensing agent. In the presence of zinc chloride a slow reaction was obtained, although the yield of sulfonefluoran was small. A maximum yield of approximately 20% of the theoretical was obtained by heating the reaction mixture for fifteen hours at a temperature of 121 to 123°. It is probable that the reaction proceeds in two steps: first, the formation of an intermediate acid and, second, the reaction of this acid with a second molecule of the cresol to form the sulfonefluoran. Since this method of preparing the sulfonefluoran is very tedious and gives low yields, it was abandoned in favor of the synthesis from the di-*p*-cresyl ester of *o*-sulfobenzoic acid, as described below.

Di-*p*-cresyl-*o*-sulfobenzoate.—This ester was prepared by the Schotten-Baumann reaction, employing *p*-cresol and the chlorides of *o*-sulfobenzoic acid (prepared by the method of List and Stein).¹⁰ To a mixture of 100 g. of *p*-cresol and 300 cc. of water in a liter flask, a strong solution of sodium hydroxide was added until the *p*-cresol was completely dissolved. The chlorides freshly prepared from 100 g. of the acid ammonium salt were added in small portions, while the temperature was kept between 30 and 35°. After the addition of the chlorides, which required about one-half hour, the mixture was allowed to stand for two hours with occasional shaking and was then boiled under a reflux condenser for two hours. During the entire series of operations the mixture was kept alkaline by the frequent addition of sodium hydroxide. The final mixture was allowed to cool and the crude ester was filtered off and recrystallized from methyl alcohol. The yield was 70%. This ester is a colorless, crystalline substance which melts at 95.5°. Professor Gill of the Department of Geology describes the crystals as

⁶ Orndorff and Sherwood, *THIS JOURNAL*, **45**, 486 (1923); Orndorff and Vose, **46**, 1896 (1924); Orndorff and Cornwell, **48**, 981 (1926); Orndorff and Purdy, **48**, 2212 (1926); S. P. Jackson, *Thesis*, "Orthocresolsulfonephthalein and Some of Its Derivatives," 1920.

⁷ Orndorff and Purdy, *THIS JOURNAL*, **48**, 2212 (1926).

⁸ Blackshear, *Am. Chem. J.*, **14**, 455 (1892).

⁹ Orndorff and Cornwell, *THIS JOURNAL*, **48**, 983 (1926).

¹⁰ List and Stein, *Ber.*, **31**, 1648 (1898).

follows. "The triclinic tabular crystals were measured but were not studied optically. The angles between the pinacoids were determined with fair accuracy as follows: 100 to 001, $89^{\circ} 1'$; 001 to 010, $117^{\circ} 59'$; 100 to 010, $73^{\circ} 54'$."

Anal. Calcd. for $C_{21}H_{18}O_6S$: S, 8.39; C, 65.93; H, 4.75. Found: S, 8.34, 8.42; C, 66.56, 66.41, 66.20; H, 5.10, 5.22, 4.97.

p-Cresyl-benzoate-*o*-sulfonechloride.—The formation of the di-cresyl ester of *o*-sulfobenzoic acid involves two consecutive reactions; first, the reaction of the acid chlorides with one molecule of the cresylate to form *p*-cresyl-benzoate-*o*-sulfonechloride and, second, the reaction of this product with a second molecule of cresylate to form the ester. At moderate temperatures the principal product is the acid chloride; considerable quantities of the ester are formed only on boiling. If the reaction mixture obtained by the addition of the acid chlorides to the cresylate (as described above) is filtered before boiling, a pasty mass consisting of impure *p*-cresyl-benzoate-*o*-sulfonechloride is obtained. This may be purified by recrystallization from glacial acetic acid. The purified material crystallized in lustrous, colorless plates which melted sharply at 138° .

Anal. Calcd. for $C_{14}H_{11}O_4S_2Cl$: Cl, 11.41; S, 10.32. Found: Cl, 11.45, 11.35; S, 10.42, 10.40.

The Sodium Salt of the Carbinolsulfonic Acid of 2,7-Dimethylsulfonefluoran.—Equal quantities of di-*p*-cresyl-*o*-sulfobenzoate and zinc chloride, together with a few drops of hydrochloric acid, were heated to 170° , with stirring, for forty-five minutes. The reaction mixture was boiled with a fairly large amount of water and filtered. The hot filtrate was made alkaline with sodium carbonate and again filtered, and the combined filtrate and washings were concentrated to a specific gravity (hot) of 1.05 and cooled. The sodium salt of the carbinolsulfonic acid of 2,7-dimethylsulfonefluoran crystallized in fine needles and was purified by two crystallizations from absolute alcohol. This product is a colorless, crystalline material, very soluble in water but insoluble in benzene or ether. It has a very bitter taste. On exposure to air and light it soon turns yellow superficially. The sodium salt is turned yellow by a mere trace of acid. Professor Gill describes these crystals as follows. "The colorless crystals show bright interference colors and parallel extinction with less optical elasticity in the direction of elongation. They are biaxial and probably monoclinic in crystal system. They show two directions of cleavage, parallel to the ends of the flattened columnar crystals, and along these cleavage planes cloudiness slowly develops as the substance is exposed to the air."

Anal. Calcd. for $C_{21}H_{17}O_6SN_2 \cdot 1\frac{1}{2}C_2H_5OH$: Na, 4.86; C_2H_5OH , 14.59. Found: Na, 4.79, 4.80; C_2H_5OH , 13.84, 14.19.

2,7-Dimethylsulfonefluoran.—By the addition of concentrated hydrochloric acid to a hot, saturated solution of the sodium salt, pure 2,7-dimethylsulfonefluoran was precipitated as a mass of fine, orange needles. The crystals were washed with cold water and dried in the air.

2,7-Dimethylsulfonefluoran chars, without melting, at about 250° . It is rather soluble in hot water but only slightly soluble in cold water. It dissolves readily in glacial acetic acid and in methyl or ethyl alcohol but does not crystallize well from these solvents. Large crystals were obtained by allowing a solution in hydrochloric acid to evaporate spontaneously. The solution in concentrated sulfuric acid has the green fluorescence characteristic of compounds containing the pyrone ring.

Professor Gill describes the crystals as follows. "The thick tabular red crystals are triclinic. In thin fragments the color is yellow with a distinct pleochroism, yellow to orange. The substance is optically biaxial with medium double refraction, the pleochroism is not observable in crystals thick enough to be blood-red in color."

Anal. Calcd. for $C_{21}H_{18}O_6S$: C, 69.19; H, 4.43; S, 8.80. Found: C, 69.08, 69.12; H, 4.52, 4.54; S, 8.81, 8.86.

Since the sulfonefluoran is colored, it is probably either an inner oxonium salt or an inner carbonium salt with *o*-quinoid or *p*-quinoid structure. There is no evidence to show which of these possible formulas is the correct one.

The P_H value of 2,7-dimethylsulfonefluoran was determined by the use of standard buffer solutions. A sharp change from yellow to colorless took place between $P_H = 9.6$ and $P_H = 10.0$. When a strong solution of sodium hydroxide was added to an aqueous solution of the sulfonefluoran a deep blue color developed immediately. This color was very transient, fading in a few seconds. Because of the instability of the blue compound it could not be isolated.

Fusion of 2,7-Dimethylsulfonefluoran with Sodium Hydroxide.—In order to verify the structure assigned to the sulfonefluoran, the products obtained by fusion with sodium hydroxide were identified. Five grams of the salt of the carbinolsulfonic acid of the sulfonefluoran was mixed with 25 g. of sodium hydroxide and 10 g. of water and the mixture was heated for two hours at 200–220°. When the fused mass was poured into water the excess alkali dissolved, leaving a residue which was identified as 2,7-dimethyl xanthone. It had a melting point of 142° and dissolved in concentrated sulfuric acid to give a solution with a blue-green fluorescence. The formation of a xanthone under these conditions is evidence of the stability of the pyrone ring in the compound. When the fusion was made at a higher temperature (280–290°) the fusion mass was almost completely soluble in water. When the solution was acidified, sulfur dioxide was evolved and, on cooling, a crop of needle-like crystals was obtained. The crystalline material was identified as parahomosalicic acid. It melted at 150° and gave an intense violet color with a solution of ferric chloride.

Action of Hydrogen Chloride, Ammonia and Bromine on 2,7-Dimethylsulfonefluoran.—The 2,7-dimethylsulfonefluoran absorbed exactly one molecule of dry hydrogen chloride. On standing over sodium hydroxide, the hydrogen chloride was given off again. The sulfonefluoran did not absorb dry ammonia. The 2,7-dimethylsulfonefluoran gives a bromine addition product of variable composition. In this respect it differs from the isomeric compound prepared by Orndorff and Purdy, which readily forms a definite dibromo derivative.

Other Derivatives.—In addition to the above described derivatives, the following were also prepared: the barium salt of the carbinolsulfonic acid, colorless needles, containing four molecules of water of crystallization (by precipitation of the sodium salt with barium chloride); the methyl ester of the carbinolsulfonic acid, fine colorless crystals, very unstable (by heating the sulfonefluoran with dimethyl sulfate); the perchlorate, fine yellow crystals (by heating a solution of the sulfonefluoran in chlorobenzene with perchloric acid).

Reduction of the Sulfonefluoran.—To a liter of boiling water containing 2 g. of zinc dust, 5 g. of the sulfonefluoran was added in small

portions. The orange color of the sulfonefluoran disappeared almost immediately after each addition. The excess zinc was filtered off and the filtrate cooled, whereupon a bulky, colorless precipitate formed. This was found to be the zinc salt of 2,7-dimethylhydrosulfofluoric acid.

Anal. Calcd. for $(C_{21}H_{17}O_4S)_2Zn$: Zn, 8.22; S, 8.06. Found: Zn, 8.10, 8.18; S, 7.99, 8.04.

The free acid was liberated by the action of concentrated hydrochloric acid on the zinc salt, but it proved to be so unstable that no satisfactory analysis was obtained. It oxidized readily in the air to the sulfonefluoran.

2'-Hydroxy-5'-methylbenzoyl-2-benzenesulfonic Acid.—The ammonium salt of this the intermediate acid, was made by the method of Ullmann and Schmidt.¹¹ Twenty-seven g. of the anhydride of *o*-sulfobenzoic acid, 25 g. of *p*-cresol and 170 cc. of acetylene tetrachloride were heated in a round-bottomed flask, connected with a reflux condenser, on an oil-bath to 100–105°. Then 60 g. of aluminum chloride was added in small portions over a period of an hour and a half, and heating continued at 105–110° for one hour longer. The fused mass was poured into water and subjected to steam distillation. The solution remaining in the flask was freed from pitch by filtration and ammonium hydroxide added to alkaline reaction. The precipitated aluminum hydroxide was filtered off, washed with hot water and the combined filtrate and washings concentrated to crystallization. The product was freed from ammonium chloride by two recrystallizations from water. Professor Gill described these crystals as follows. "The larger stout columnar crystals and the finer (blade-like) needles show parallel extinction. This suggested rhombic crystallization but measurements of the angles on a reflecting goniometer by Dr. D. W. Trainer show that they are doubtless monoclinic elongated in the direction of the ortho axis probably of axial sphenoidal (sphenoidal, Groth) symmetry, since the ends seem to show good faces at only one extremity. The approximate angles in the zone of the ortho axis may be given as 30° 9', 60° 19', 38° 6' and 51° 26', and the angle between the end faces is 62° 34'. Double refraction is very strong and the biaxial character is certain."

Anal. Calcd. for $C_{14}H_{11}O_6SNH_4$: S, 10.37; N, 4.53. Found: S, 10.55, 10.46; N, 4.57, 4.58.

The free intermediate acid was obtained from the ammonium salt in the following manner. The ammonium salt was suspended in anhydrous ether and dry hydrogen chloride passed in, keeping the temperature below 10°. The ammonium chloride was filtered off and the ethereal solution quickly evaporated to dryness. A sirup resulted which solidified in a few hours. When this solid was dried on a porous plate, a crystalline powder was obtained. The intermediate acid has a melting point of 90°. It is unstable, decomposing to *p*-cresol and *o*-sulfobenzoic anhydride. Fused with potassium hydroxide it yields *p*-homosalicylic acid, the substance which was obtained from the sulfonefluoran under similar conditions. Heated with *p*-cresol the intermediate acid reacts to form 2,7-dimethylsulfonefluoran.

Anal. Calcd. for $C_{14}H_{12}O_6S$: Mol. wt., 292.16; S, 10.97. Found: Mol. wt., 291.6, 294.7, 298.9; S, 10.89, 11.01.

2,7-Dimethylsulfonecoeroxonol.—Ten g. of the sulfonefluoran was dissolved in 200 g. of concentrated sulfuric acid and the solution was heated at 200° for two hours. The cooled solution, which was deep red, was poured into 200 g. of ice. A small amount of insoluble matter was then filtered off and the solution was added to a mixture of am-

¹¹ Ullmann and Schmidt, *Ber.*, 52, 2098 (1918).

monium hydroxide and ice. A bulky, brownish precipitate resulted which was filtered off, washed and dried. This substance resembles the coeroxonols made by Ferrario.¹² It is insoluble in water and ether, somewhat soluble in benzene, xylene and alcohol and very soluble in acids, with an intense red color. Hence it was called 2,7-dimethyl-sulfonecoeroxonol.

Anal. Calcd. for $C_{21}H_{16}O_4S$: S, 8.80. Found: S, 8.65, 8.63.

Summary

The results of this investigation may be summarized as follows.

1. 2,7-Dimethylsulfonefluoran has been prepared both by the condensation of *o*-sulfobenzoic anhydride with *p*-cresol and by the fusion of di-*p*-cresyl-*o*-sulfobenzoate with zinc chloride. The latter method gave the better yield.

2. 2,7-Dimethylsulfonefluoran is a colored substance and hence is supposed to have a quinoid structure. It may be represented either as an inner oxonium or inner carbonium salt.

3. On fusion with sodium hydroxide, 2,7-dimethylxanthone and *p*-homosalicylic acid are produced. The formation of these substances is in accord with the structure assigned to the sulfonefluoran.

4. Unlike fluorans and the only other sulfonefluoran mentioned in the literature, 2,7-dimethylsulfonefluoran forms salts and esters. The sodium and barium salts and the methyl ester have been prepared. These are derived from the carbinolsulfonic acid form of the fluoran and are colorless.

5. Two derivatives of the colored form have been prepared, the hydrochloride and the perchlorate.

6. 2,7-Dimethylsulfonefluoran behaves as an indicator. The change from yellow to colorless takes place at a *P_H* of 9.6–10.0.

7. 2,7-Dimethylhydrosulfofluoranic acid has been made by the reduction of the sulfonefluoran. This compound is colorless.

8. The intermediate acid, 2'-hydroxy-5'-methylbenzoyl-2-benzene-sulfonic acid has been made by the Ullmann and Schmidt method, which consists in condensing *o*-sulfobenzoic anhydride with *p*-cresol in acetylene tetrachloride in the presence of aluminum chloride. The acid is unstable, decomposing to give *p*-cresol and the anhydride of *o*-sulfobenzoic acid.

9. Heating the sulfonefluoran with sulfuric acid causes the elimination of a molecule of water with the formation of 2,7-dimethylcoeroxonol.

ITHACA, NEW YORK

¹² Ferrario, *Ann.*, **348**, 213 (1906).