determination of hydrates.[1] In this work, the authors determined, as we did, the solubility of copper sulfate in sulfuric acid solutions at 25° and Professor Bell has now recalculated the solubility results to a common basis and finds our results confirm his earlier ones. The composition of the hydrates in equilibrium with the solutions was determined by Bell and Taber by the method of residues and graphical extrapolation. We obtained the residues free from mother liquor by treatment with alcohol, depending on the composition of the solutions in a series of determinations for information as to whether the residues thus obtained were pure hydrates or mixtures of two. Both investigations show the presence of the same hydrates. Bell and Taber also calculated the approximate vapor pressures of the hydrates from the vapor pressures of the solutions, a point which we briefly considered without knowing of their work.

H. W. FOOTE.

The Stannic-Stannous Potential.—Mr. H. W. Richter, at present collaborating with one of us, has kindly called our attention to an error in our paper entitled "The Measurement of Oxidation Potentials at Mercury Electrodes. I. The Stannic-Stannous Potential," THIS JOURNAL, **36,** 2035 (1914). Owing to neglect of the temperature coefficient of the normal calomel electrode, its electromotive force at 25° was assumed as 0.560 instead of 0.564 volt. Therefore, 0.004 volt must be added to each of the single potentials recorded, and the value of the stannic-stannous potential at 25° becomes

$$\pi = 0.430 + 0.030 \log \frac{Sn^{IV}}{Sn^{II}} - 0.011 \times \text{conc. HCl}.$$

GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THE ORCINOLPHTHALEINS, THE ORCINOLTETRACHLOROPHTHALEINS, AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND E. R. ALLEN.

Received March 9, 1915.

Historical.

Orcinolphthalein was first made and studied by Emil Fischer,[2] working under the direction of A. von Baeyer at Strassburg, and the results published as his inaugural dissertation in 1874. He obtained small amounts of this phthalein by heating orcinol and phthalic anhydride to 210–220°. Much better results were obtained by heating freshly fused anhydride, distilled orcinol and concentrated sulfuric acid for two hours to 135°.

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[1] THIS JOURNAL, **37,** 288 (1915).

[2] *Ann.* (Liebig), **183,** 63 (1876).

Final purification was effected by crystallization from acetone or from glacial acetic acid. The analyses of the product dried at 180° agreed with the formula $C_{22}H_{16}O_5$, and a structure analogous to that held for fluorescein at that time was proposed for it.

Dilute alkalies and ammonia dissolve it readily with an intensely dark red color. The solutions of the pure substance show no fluorescence, those of the crude product only a faint greenish fluorescence.

The phthalein showed no melting point, decomposing at about 230°. By boiling the phthalein with acetic anhydride he obtained a colorless product, insoluble in alkalies, which gave results on analysis for the diacetyl derivative. It is completely analogous to diacetyl fluorescein, and melts at 219–220°.

According to Fischer the behavior of orcinolphthalein toward glacial acetic acid is peculiar; for, while with care it can be crystallized in short, perfectly colorless prisms, if the solution be heated for some time the crystals suddenly turn yellowish red, and even by repeated crystallization they cannot again be obtained colorless. This colored compound dissolves in alkalies with the same color as the pure phthalein, but is precipitated unchanged by acetic acid. Before the reason for this phenomenon was understood the purification of the phthalein was rendered unusually difficult, since at one time colorless crystals were obtained from acetic acid, while at another they were red. Further investigation led Fischer to conclude that this conversion was caused by the acetic acid itself. By heating the phthalein with acetic acid in a sealed tube to 150° he obtained a compound, which, on analysis gave results approximating those required for a monoacetyl derivative, *i. e.*, $C_{22}H_{15}O_5(C_2H_3O)$.

Calculated: C, 71.64; H, 4.47; found: C, 72.13; H, 4.46.

The high carbon content found he attributes to a slight admixture with the phthalein (see p. 1205).

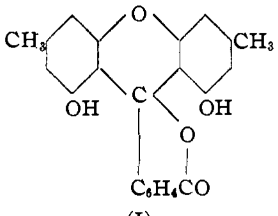
As an example of the dark red compounds which orcinolphthalein forms with mineral acids Fischer isolated and analyzed the hydrochloride. Even in the cold hydrochloric acid colors the white phthalein red, but for complete conversion an excess of hydrochloric acid is added to an alcoholic solution of the phthalein, which becomes colored dark red. On evaporating the alcohol, the compound separates in dark red flocks. These were dried in a vacuum over sulfuric acid. They then analyzed in close agreement with the formula $C_{22}H_{16}O_5.HCl$.

On the addition of bromine in excess to the boiling glacial acetic acid solution of the pure phthalein, the tetrabrom substitution product was obtained. Its solution in alkalies has an almost black color, which on dilution becomes dark brown, and shows a peculiar blackish green fluorescence (see p. 1207). In regard to the positions occupied by the bromine atoms Fischer points out that they are probably equally distributed between the two orcinol residues, since each of these contains but two hydrogens in the benzene nucleus.

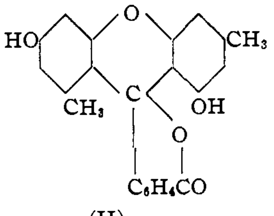
Baeyer and Fischer point out, in conclusion, that a comparison of fluorescein with orcinolphthalein shows that, in spite of their analogous constitution, they show surprising differences in physical and chemical properties.

Later[1] Richard and Heinrich Meyer took up the study of orcinolphthalein to see if an explanation for this great lack of analogy between orcinolphthalein and fluorescein could be found. The differences were mainly that orcinolphthalein is only formed with condensing agents, and that it dissolves in alkalies with a carmine red color without fluorescence. Orcinolphthalein then resembles more closely in its formation and properties phenolphthalein than fluorescein.

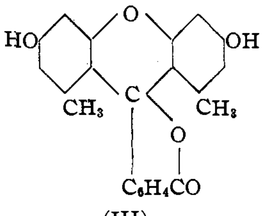
As in the investigation of hydroquinonephthalein[2] they determined whether the orcinolphthalein contained an anhydride oxygen as firmly bound in a ring as in the case of fluorescein, by benzoylating in alkaline solution, assuming that if the phthalein contained a pyrone ring a dibenzoate would be formed, but, if a less stable anhydride ring were present, during the benzoylating it would be ruptured and a tetrabenzoate would result in consequence of the formation of two new hydroxyl groups. Experiment decided the question in favor of the first assumption. Orcinolphthalein prepared according to the method of Fischer gave a well characterized dibenzoate by the Schotten-Baumann reaction, a direct benzoyl determination proving beyond a doubt that the formula was $C_{22}H_{14}O_5$-$(C_7H_5O)_2$. In purifying this dibenzoate, however, R. and H. Meyer obtained two other benzoates, which could be only incompletely separated by means of solvents, one of which, on saponification, gave a cherry-red, the other a green fluorescent solution. This led to the conclusion that in the crude orcinolphthalein a mixture of the three possible structural isomers existed.



(I).



(II).



(III).

This assumption was proved correct by their subsequent work. The third formula belongs undoubtedly to the fluorescent substance, which is a true fluorescein, giving on bromination an eosin, but which formula to

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[1] *Ber.*, **29**, 2627 (1896).

[2] *Ibid.*, **28**, 2959 (1896).

assign to each of the other two isomers they were unable to decide. To distinguish between the three isomers they designate the product of Emil Fischer,[1] soluble in alkalies with a carmine red color as α, the one soluble in alkalies with a cherry-red color as β, and the one soluble with fluorescence as γ.

They state that as a result of experiments with different condensing agents they found that sulfuric acid, zinc chloride, tin tetrachloride, phosphorus pentoxide, or ferric chloride gave a product consisting chiefly of approximately equal parts of the α- and β-compounds, with only subordinate amounts of the γ-, while if glacial phosphoric acid be used the γ-product was obtained in relatively better yields (see p. 1215).

For separating the isomers they depended on their different behavior towards alkalies. α-Orcinolphthalein is soluble only in caustic alkalies, but not in ammonia or the alkali carbonates; the β-compound dissolves easily in the latter also, but not in a solution of ammonium sesquicarbonate; γ-orcinolphthalein unites even with ammonia gas to form an ammonium salt easily soluble in water.

In the experimental part of their paper the authors state that the best way to obtain the crude product is to follow the directions of Emil Fischer, and add, that if, instead of concentrated sulfuric acid as a condensing agent, phosphorus pentoxide be used a better yield of the γ-isomer is obtained.

The crude fused mass was poured into cold water, and the orange colored precipitate dissolved in sodium hydroxide. The mixture of the three phthaleins was precipitated by dilute sulfuric acid, and washed free from inorganic impurities by means of hot water. The residue was then dried at 120°, finely ground and treated under a bell jar with gaseous ammonia for some hours. By means of water the ammonium salt of the γ-phthalein was dissolved with a brown color and greenish fluorescence. From the residue, dilute ammonium sesquicarbonate (1 : 15) dissolves the remainder of the γ-compound, leaving only the α- and β-phthaleins, and from this mixture cold soda solution removes all the β-compound, leaving almost pure α-phthalein.

They observe that this separation is not absolutely sharp, especially when working with large amounts of material, but it sufficed for the preliminary work, since each compound was further purified as described below.

α-Orcinolphthalein.—Besides the above described method, this isomer was obtained by washing the crude product with aqueous ammonia till the latter was no longer colored cherry-red but bluish red. The residue is almost pure α-phthalein and gives at once colorless crystals from glacial acetic acid. These they considered to be pure if their solution in soda was

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[1] Fischer's product was probably a *mixture* of α- and β-orcinolphthaleins (see pp. 1205, 1206 and 1207).

completely decolorized by shaking with ether or remained only faintly bluish red, not cherry-red. Potassium and sodium hydroxides dissolve the α-phthalein readily with a bluish red color. It dissolves in cold ammonia only slightly, and in soda solution only on warming, and even then with difficulty, with the same color. The solutions in ammonia and soda are decolorized on shaking with ether, whereupon the phthalein goes into the ether. Contrary to expectation, a very dilute potassium hydroxide solution acted in the same way (see p. 1225). In all cases a colorless ether solution resulted which, on evaporation, left the free colorless phthalein, and which gave up the phthalein again when treated with concentrated caustic alkali with the production of a red color. This behavior shows the extremely weak acid nature of the α-phthalein. By mixing an alcoholic solution of the phthalein with alcoholic potassium hydroxide a blue potassium salt separated in clusters of small needles having a bronzy luster (see p. 1208).

The red hydrochloric acid addition product described by E. Fischer was also obtained by R. and H. Meyer, from the *pure α-phthalein* but was not isolated or analyzed by them.

The brown "*monoacetate,*" mentioned by Fischer (see p. 1202) as formed by heating his phthalein with glacial acetic acid, was never observed by R. and H. Meyer. Heating the α-phthalein with glacial acetic acid in a sealed tube to 150–180° gave them only colorless crystals of the phthalein. They state that the analyses of E. Fischer, as well as his description of the conduct of his *so called monoacetate*, agree so well with those of the β-phthalein described below that it is very probable the two compounds are identical (see p. 1206).

Tetrabromo-α-orcinolphthalein was prepared by dissolving pure α-phthalein in hot glacial acetic acid, and treating with the calculated amount of bromine. The yellow needles which separated were obtained from hot nitrobenzene as flat, yellow prisms which analyzed in agreement with the formula $C_{22}H_{12}Br_4O_5$. These dissolve in alkalies with a violet color, which on heating becomes stronger and pure blue. On cooling the reddish blue color returns (see p. 1220).

β-Orcinolphthalein.—The β-phthalein is found in the cherry-red solution obtained by extracting the crude material, from which most of the γ-compound had been removed, with soda. From this solution acids precipitate a bright yellow compound, which was purified by dissolving in ammonia, precipitating with sufuric acid, and washing with water. The residue was dissolved in alcohol and hot water added until the liquid becomes turbid. On further heating this disappears, and the formation of crystals begins. As soon as these separated the solution was filtered while still warm, in order that any γ-compound remaining might be held in solution. This crystallization was repeated, until the dried crystals when treated with gaseous ammonia neither changed their color nor gave a fluorescent solution on the addition of water. The crystals thus obtained were mostly a mixture of more or less brownish needles and orange-colored leaflets, which, however, in both cases were pure β-orcinolphthalein (see p. 1227). In order to obtain them all as needles a dilute (1 : 20) alcoholic solution of the phthalein is run while hot into ten times the amount of cold water, and digested on the water bath till the milky white turbidity has been converted into clusters of microscopic needles. If, on the other hand, the phthalein be dissolved in ten times the amount of hot alcohol, one-half the volume of water added to this, and the solution boiled, fairly large, orange-colored, six-sided plates separate. These lose no water *even at 205°*, and decompose at higher temperatures. Although this residue gave data on combustion in agreement with the formula for the anhydrous phthalein, the authors state: "dieselbe kann aber unter den obwaltenden Unständen kaum als entscheidend angesehen werden." Four other combustion analyses are given, 1 and 2 are on the leaflets obtained by the addition of water to the alcoholic solution, 3 is on the amorphous material precipitated from the alkaline solution by sulfuric acid, and finally 4 is on the phthalein recovered from the β-phthaleindibenzoate, and which had been dissolved in alcohol and crystallized by heating with water. In 1 and 2 the substance was dried in a xylol bath, and in 3 and 4 in an aniline bath. The analyses agree with the formula $C_{22}H_{16}O_5.{}^1/_3H_2O$ (see p. 1428).

Calculated: C, 72.13; H, 4.55; found: C (1) 72.01, (2) 72.10, (3) 71.98, (4) 72.13; H, (1) 4.50, (2) 4.49, (3) 4.23. (4) 4.37.

These analyses are in agreement with those given by E. Fischer for his "*monoacetate*" (see p. 1202), and the following observations according to R. and H. Meyer also prove the identity of the two: If the needle-shaped crystals of the β-phthalein be dissolved in glacial acetic acid by gently warming, then on cooling almost colorless needles separate; if, on the other hand, the solution be boiled strongly, yellowish red leaflets crystallize out on cooling. From dilute alkaline solutions this phthalein is thrown down as a *white* precipitate by acetic acid (see p. 1229).

The β-phthalein does not show a definite melting point. It is easily soluble with a brown color in methyl and ethyl alcohols, and in ethyl acetate, difficultly soluble in hot water, benzene or glacial acetic acid. Ether dissolves the amorphous substance easily. It dissolves in caustic alkalies and their carbonates, as well as in ammonia, with an intense cherry-red color, which even in extreme dilution does not disappear on shaking with ether. Mineral acids precipitate the free phthalein out of this solution in yellow flocks. Solutions of sodium phosphate or sodium acetate also dissolve it, on warming, with a cherry-red color, but this color disappears on shaking with ether, which takes up the phthalein.

With fuming hydrochloric acid the β-phthalein forms a deep red addition product insoluble in hydrochloric acid similar to that of the α-isomer (see p. 1205).

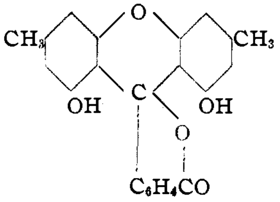
Tetrabromo-β-orcinolphthalein was obtained by boiling the β-phthalein with glacial acetic acid and the calculated amount of bromine. Brown crystals separated. These were washed with alcohol, dissolved in sodium hydroxide, precipitated with sulfuric acid, the precipitate washed with water, and extracted with alcohol. The white crystalline residue gave, on recrystallization from hot nitrobenzene, irregular colorless plates. These gave results on analysis agreeing with the formula $C_{22}H_{12}Br_4O_5$. It dissolves with difficulty in all solvents except hot nitrobenzene. Caustic alkalies and the alkali carbonates dissolve it with a greenish black color; when very dilute this solution shows by transmitted light a smudgy red color. R. and H. Meyer point out that this description agrees so well with that given by Emil Fischer (see p. 1202) for his tetrabromoorcinolphthalein that there can be no doubt that it was actually the tetrabromo-β-orcinolphthalein with which he was working. The substance is not a dye. Gaseous ammonia does not act on it, and hence it may be easily isolated from a mixture of tetrabromo-β- and -γ-orcinolphthaleins (see p. 1232).

γ-Orcinolphthalein.—To isolate this body the crude product was treated with gaseous ammonia, extracted with water, and the resulting solution allowed to stand in the air for some time, when some β-phthalein precipitated. This was filtered off and from the filtrate the γ-phthalein was precipitated by sulfuric acid. This was washed with hot water, dissolved in ammonia, alcohol added, the solution acidified with sulfuric acid and steam passed into the milky solution to remove the alcohol. On cooling, tolerably large, pale yellow prisms separated. From hot, concentrated, glacial acetic acid solution dark orange-colored crystals separated on cooling. The analyses of the two products dried at 180° were in accord with the formula $C_{22}H_{16}O_5$ (see p. 1235).

The γ-orcinolphthalein is easily soluble with a brown color in alcohol, methyl alcohol, and hot glacial acetic acid. From dilute alcohol it separates on slow evaporation in bright yellow clusters of broad, truncated needles. It exhibits the greatest analogy to fluorescein. When precipitated in the amorphous form it is deep yellow colored, and dissolves in alkalies, ammonia, and their carbonates with a brown color and greenish fluorescence. This is not so intense as in the case of fluorescein, but is considerably increased by the addition of alcohol. The substance dyes silk yellow. It dissolves on heating in sodium phosphate and sodium acetate solutions, presumably due to the formation of the sodium salt (as in the case of fluorescein). These solutions fluoresce, and are not decolorized on shaking with ether (distinction from β-orcinolphthalein). On boiling with calcium carbonate, carbon dioxide is expelled and the substance goes into solution as the calcium salt. When boiled with hydrochloric acid or dilute sulfuric acid small amounts of it dissolve with a yellow color. The amorphous substance is easily soluble in ether with a yellow color and without fluorescence. The ammonium salt forms readily under the action of gaseous ammonia, as mentioned above. The ammonia passes off completely from this compound, however, on long exposure to the air.

In his paper on "Untersuchungen über die Abkömmlinge des Triphenylcarbinols,"[1] Baeyer gave some attention to the α-orcinolphthalein of R. Meyer. As will be shown below he concludes that in this isomer the hydroxyl groups occupy the positions ortho to the methane carbon atom. He proposes to replace the designation α- with the term vicinal, since it is customary to designate the volatile nitroresorcinol of Kauffman in which the nitro group occupies an analogous position as vicinal nitroresorcin. The mother substance, which has, however, not yet been made, would then be designated as *vic*-resorcinolphthalein, and likewise the triphenylcarbinol derivative as *vic*-resorcinolbenzein. For the β-orcinolphthalein of R. Meyer which is an intermediate product between the vicinal and the ordinary form, he proposes the term semi-vicinal, to be shortened to "semi-vic," while the γ-substance is to be designated simply as orcinolphthalein.

According to Baeyer the *vic*-orcinolphthalein corresponds so exactly in its conduct to the *vic*-nitroresorcinol, that it must possess the structure given below:



Vic-orcinolphthalein.

He calls attention to the fact that Meyer's statement (see p. 1205) "Beim Vermischen einer alkoholischen Lösung des Phtaleins mit alkoholischen Kali, bildet sich ein in alkohol unlösliches blaues Kaliumsalz, das in kleinen bronzeglänzenden Nadelbüscheln ausfällt" is incomplete. According to Baeyer, if a little alcoholic potash be added to an alcoholic solution of the vicinal orcinolphthalein, the solution is at first colored violet, but this soon disappears, and a potassium salt separates in colorless, elongated, right-angled plates. This salt, Baeyer states, may be used advantageously for the complete separation of the vicinal orcinolphthalein from its isomers. For if it be heated with a large amount of water the salt is decomposed by hydrolysis into the free orcinolphthalein and into alkali, which holds a small part of the vicinal orcinolphthalein and all of

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[1] *Ann.* (Liebig), **372**, 120 (1910).

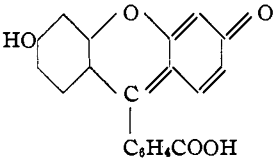
its isomers in solution. The *vic*-orcinolphthalein when filtered off is pure white, and is completely extracted from its red solution in soda on shaking with ether.

If more alcoholic potash be added to the solution of the phthalein (from which the white crystals of the potassium salt have separated), and the solution be boiled it becomes a deep reddish violet, and crystals separate which appear black under the microscope, but which possess the same forms as the white, *i. e.*, are apparently pseudomorphs. If, however, the alcoholic solution of the phthalein be added to an excess of alcoholic potash heated to boiling, black needles, obliquely truncated, separate. Besides these, blue, transparent leaflets are also formed.

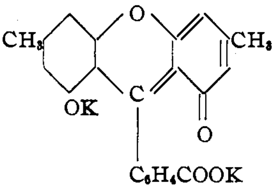
When the white crystals are boiled with soda solution, there separates on cooling, hair-like needles of a violet color, but, if they are warmed with concentrated potassium hydroxide, the liquid becomes pure blue. On dilution the solution turns violet.

From this Baeyer concludes that there are at least three kinds of salts, a white, a red, and a blue, the formation and composition of which he accounts for in the following manner:

From the formula for the vicinal orcinolphthalein (see p. 1208), it would be simplest to assume that, in the first place, the hydrogen atoms of the two hydroxyl groups are replaced by metal. Such a salt must, however, be colorless. Since now a violet color first appears, it is to be assumed that in the first place the rupture of the lactone ring takes place with the formation of a violet salt, corresponding to fluorescein, which, however, contains instead of a para- an ortho-quinoid group.

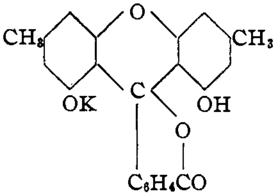


Fluorescein.



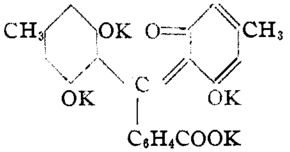
First violet salt.

This first violet salt changes into the colorless, monopotassium salt of the phthalein through reformation of the lactone ring, which, as the decolorization of an alkaline solution by means of ether shows, takes place very readily in the case of the vicinal orcinolphthalein.



Colorless salt.

On the addition of more alkali the lactone group is broken again, and there is formed in consequence of this a tertiary alcohol, to the active nature of which is to be attributed the rupture of the xanthone ring. That this rupture actually takes place even at ordinary temperature is shown by the analysis of the colored potassium salt, according to which it contains between 3 and 4 atoms of potassium. This is possible, however, only on the assumption of the hydrolytic cleavage of the oxygen bridge. The colored salt containing four atoms of the metal can only have the following constitution because of the symmetrical structure of the orcinol:

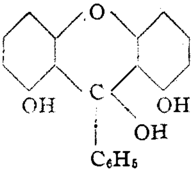


since it is immaterial, whether the hydroxyl already present or that formed from the bridge oxygen becomes quinoid. Analyses of the potassium salts (see pp. 1222 to 1227):

1. Colorless potassium salt:[1] calc. for $C_{22}H_{14}O_5K_2$: K, 17.89; for $C_{22}H_{14}O_6K$: K, 9.37; found: K, 13.64.

2. Blue potassium salt: calc. for $C_{22}H_{14}O_6K_4$: K, 29.43; found: K, 27.05.

In regard to the analogy between phenyl-2,2′-dioxyxanthanol (*vic*-resorcinolbenzein)



and α-orcinolphthalein Baeyer says:[2]

"Aus der Identität der Färbung, welche das Chlorid in Alkalischer Lösung zeigt, mit der des α-orcinphtaleins von R. Meyer, geht hervor, dass letzteres wirklich, wie angenommen, *vic*-orcinphtalein ist."

Recently Kehrmann[3] has prepared ethers and esters of the phthaleins and benzeins of orcinol with a view to studying their oxonium salts.

In order to completely free the β-phthalein from the tenaciously adhering γ-isomer, Kehrmann dissolves the crude β-compound (isolated according to the method of R. and H. Meyer) in boiling alcohol, adds a few drops of ammonia, and then boiling water until the solution becomes

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[1] The formula for the monopotassium salt is $C_{22}H_{15}O_5K$, and according to 1915 atomic weights contains 9.82% potassium; that of the dipotsssium salt $C_{22}H_{14}O_5K_2$, and 17.92% potassium; that of the tetrapotassium salt $C_{22}H_{14}O_6K_4$, and 29.48% potassium. The tripotassium salt of the *carbinol carboxylic acid*, $C_{22}H_{15}O_6K_3$, contains 23.82% potassium (see p. 1227).

[2] *Ann.* (Liebig), **372**, 133 (1910).

[3] *Ber.*, **45**, 3505 (1912).

turbid. During the cooling the β-isomer crystallizes out, while the mother liquor shows the presence of the γ-compound by its fluorescence. Repeated three times this method gave a product which no longer yielded a fluorescent mother liquor when treated in this manner, and was, therefore, certainly free from the γ-isomer.

Kehrmann states that β-orcinolphthalein exists in *two modifications, a yellow quinoid, and a colorless lactoid form,* and he adds in a footnote that R. and H. Meyer had already observed both modifications, but that it was not quite certain whether their product was perfectly free from the γ-isomer (see p. 1228). Acidification in the cold of the dark brownish red alkaline solution gives, according to him, an orange yellow precipitate, which when heated to boiling becomes perfectly white. The lactoid form is here the stable one, while the salts, those with alkalies as well as those with acids, are derived from the quinoid modification, which is unstable in the free condition (see p. 1229). The latter form becomes the stable one, however, by esterifying the carboxyl or by replacing it with hydrogen, as the study of γ-orcinolbenzein has shown.

In order to completely free the γ-isomer from traces of the tenaciously adhering β-derivative, Kehrmann states that treatment of the crude product with methyl alcohol and hydrochloric acid was found to be very advantageous. The hydrochloride, which separated quite completely in bright orange-yellow leaflets having a bluish reflection, was chemically pure. In a footnote he states that the base exists in a yellow and in a colorless form (see p. 1234).

Experimental.

The investigation of the orcinolphthaleins and of the orcinoltetrachlorophthaleins was undertaken (1) to study the effect of introducing negative groups into the phthalein molecules; (2) to observe to what extent these compounds and their derivatives exist in colored and colorless modifications, and to see whether these forms are in agreement with the theory of color held by chemists at the present time; and (3) to study the conditions affecting the formation of the different isomers, and the methods of separating these, thus throwing possible light on the problem of the isomeric fluoresceins.[1]

At the outset some difficulty was encountered in preparing the orcinoltetrachlorophthaleins (see p. 1239). This difficulty, together with the fact that R. and H. Meyer had not carefully studied the colored and colorless forms of the orcinolphthaleins, and had omitted certain important derivatives prompted the repeating and enlarging of the major part of the work previously done on these phthaleins.

The phthalic anhydride used in this work was pure sublimed material. The orcinol obtained from Merck was pure and had a melting point of

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[1] THIS JOURNAL, 36, 680 (1914).

58°. It was freshly fused before using. The fused material[1] melted sharply at 107°.

In the preparation of the orcinolphthaleins the directions of E. Fischer were first employed. Fifty grams of phthalic anhydride, 85 g. of orcinol, and 45 cc. of concentrated sulfuric acid were placed in a flask and heated to 135° for two hours. The mass became semi-liquid, and red colored, but did not solidify toward the end of the reaction. It was poured into water, the yellowish incoherent mass filtered, washed, and the filtrate preserved for the recovery of unchanged orcinol. The material was then dissolved in alkali, the solution filtered, the phthaleins precipitated as a yellowish flocculent mass with acetic acid, and the mixture heated to boiling by blowing in steam. The material darkened slightly and showed a tendency to collect in pasty masses. The anhydrous material weighed 104.5 g., corresponding to 85.9% of the theory, calculated from the amount of phthalic anhydride used.

Fifty grams of this material were purified (see pp. 1216 and 1217) and the following amounts of isomers obtained:

Isomer.	Grams.	Percentage.
α	10.0	23.0
β	27.0	62.2
γ	5.4	12.5
Tar	1.0	2.3
Total	43.4	100.0

The use of phosphorus pentoxide at 135° as a condensing agent was next tried. One hundred grams phthalic anhydride, 170 g. orcinol, and 170 g. phosphorus pentoxide were placed in a flask and heated to 135° for two hours. The dark red mass was ground, dissolved in alkali, and the solution filtered. The phthaleins were then precipitated by adding dilute sulfuric acid, and the mixture heated to boiling with steam, filtered and washed in the usual manner. This product differed markedly from that of the previous fusion in that it became dark, almost black, on heating to boiling with steam, and collected in a sticky mass which on drying became hard and brittle. The crude anhydrous material weighed 140 g., corresponding to 57.5% of the theory.

Fifty grams of this material were purified, and resolved into its isomers:

Isomer.	Grams.	Percentage.
α	5.0	11.9
β	21.0	50.0
γ	14.0	33.3
Tar	2.0	4.8
Total	42.0	100.0

The synthesis was repeated, keeping the temperature between 180° and 190°. The material from this fusion was purified as usual. It was precipitated from the alkaline solution as yellow flocks by the addition of mineral acids. On heating this mixture to boiling with steam the material became dark colored and collected in a pasty mass.

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[1] The statement of Hesse, *J. prakt. Chem.*, [2] **57**, 270, that the melting point of *anhydrous* orcinol is 100–101°, is certainly incorrect. We have determined this melting point many times and on large quantities of material, and have invariably found it to be 107°.

Fifty grams phthalic anhydride, 87 g. of fused orcinol and 90 g. of P_2O_5 gave 87 g. of anhydrous material corresponding to a yield of 71.5%.

Fifty grams of this material gave on purification:

Isomer.	Grams.	Percentage.
α	5.7	13.2
β	22.0	50.9
γ	14.0	32.4
Tar	1.5	3.5
Total	43.2	100.0

Sulfuric acid at a high temperature was then used as a condensing agent. The bath was heated to 180–190°, and the flask containing 25 g. phthalic anhydride, 43 g. orcinol, and 23 cc. of concentrated sulfuric acid was immersed in it for two hours. The reaction was vigorous, and was accompanied by boiling. The temperature of the mixture showed a tendency to rise above 180° as a result of the heat of the violent reaction. A too high rise was avoided by removing the flask occasionally from the bath. The melted mass was poured into water, and purified in the usual manner. The phthaleins were precipitated from the alkaline solution with sulfuric acid as yellow flocks, which when heated to boiling by blowing in steam darkened but slightly, and showed but little tendency to form pasty masses. The yield of anhydrous material was 92.5%. The entire product (55.5 g.), gave the following amounts of the different isomers:

Isomer.	Grams.	Percentage.
α	14.7	28.2
β	29.4	56.4
γ	7.6	14.6
Tar	0.4	0.8
Total	52.1	100.0

Meyer states that (see p. 1204) glacial phosphoric acid gives a larger yield of the γ-isomer. This substance was therefore used as a condensing agent. Twenty grams phthalic anhydride, 39 g. orcinol, and 60 g. glacial phosphoric acid were ground together and heated. The reaction took place very slowly even at 195–200°. At the end of two hours the heating was discontinued and the fused mixture freed from unchanged orcinol, phthalic anhydride, and inorganic materials in the usual manner. On heating to boiling with steam the product was obtained as a black, tarry mass, which on drying became hard and brittle. The anhydrous material (27.6 g.) corresponded to a yield of 56.7% of the theory (see p. 1215).

A smaller amount of phosphorus pentoxide was next tried to see if the production of tar could be avoided. Twenty grams phthalic anhydride, and 34 g. orcinol were fused at 180°, and the condensing agent, 13 g. P_2O_5, then added. The temperature was maintained at 180° for two hours, and the product of the fusion was purified in the usual manner. Upon the addition of an acid to an alkaline solution of the crude material a yellowish brown flocculent precipitate was obtained which blackened and formed a pasty mass on heating to boiling. A yield of only 52.8% was obtained by this method. The experiment failed, therefore, to accomplish the desired end.

The experiment was repeated at a temperature of 120°. While the crude product was free from tar, *i. e.*, precipitated as *yellow* flocks, which remained unchanged on heating to boiling, only 9 g. corresponding to a yield of 18.5%, was obtained. On separation this product yielded the following amounts of isomers:

Isomer.	Grams.	Percentage.
α	1.2	13.8
β	5.0	57.5
γ	2.5	28.7
Total	8.7	100.0

The experiment was again repeated but the temperature maintained at 135°. The crude anhydrous phthaleins which contained some tar, weighed 15 g., corresponding to a yield of 30.8%.

Fuming sulfuric acid was next tried as a condensing agent. Twenty grams phthalic anhydride, 34 g. orcinol, and 18 cc. fuming sulfuric acid (15% SO_3) were used. The first two were fused at 120°. The fuming sulfuric acid was then added, and a vigorous reaction took place at once, accompanied by change of color, boiling, and evolution of steam. The flask was quickly removed from the bath, but the temperature continued to rise, finally reaching 200°, but on being left to stand at room temperature returned to 120° in 20 minutes. The flask was then replaced in the bath and the temperature of the contents held at 120° for two hours. The melted mass, which showed no tendency to solidify, was poured into water. The lumps which formed at once were easily broken up, and the whole mass soon became yellow and pulverulent. When dissolved in alkali and subsequently precipitated with mineral acids it separated as bright yellow flocks, which on heating to boiling with steam did not change in the least, *i. e.*, it was perfectly, free from tar. The material was filtered off, washed, and dried to constant weight in the water oven. After this treatment it weighed 47.5 g., 97.9% of the theory.

The product was next resolved into its isomers by the usual method. It was found to be so nearly free from tar that on filtering the ether solution (see p. 1217) only enough was present to color the filter paper slightly. The entire 47.5 g. gave:

Isomer.	Grams.	Percentage.
α	11.7	27.4
β	25.0	58.5
γ	6.0	14.1
Total	42.7	100.0

This synthesis was repeated using the same amounts of materials. The reaction took place slowly even at room temperature, the contents of the flask turning red, and the temperature in a few minutes rising to 75°. The flask was then immersed in boiling water for four hours. The content was stirred by an occasional shaking. The purification was carried out exactly as in the preceding experiment, and the product was exactly similar in all respects. The anhydrous material weighed 47.5 g., 97.9% of the theory. Separated into its isomers the following results were obtained:

Isomer.	Grams.	Percentage.
α	11.0	25.9
β	25.0	58.8
γ	6.5	15.3
Total	42.5	100.0

Zinc chloride was finally used as a condensing agent. Twenty grams phthalic anhydride, 34 g. orcinol, and 34 g. freshly fused zinc chloride were intimately ground in a mortar, transferred to a flask, and heated to a temperature of 120° for two hours. The mass became red in color and semi-liquid, and at the end of two hours had partially solidified. Purified as in previous cases the material (24.7 g.) was found to be practically free from tar. The yield was, however, only 50.8% of the theory.

SUMMARY OF IMPORTANT SYNTHESES.

Condensing agent.	Temperature.	Crude yield. %	Percentage Isomers.		
			α.	β.	γ.
P_2O_5	135°	57.5	11.9	50.0	33.3
P_2O_5	180°	71.5	13.2	50.9	32.4
P_2O_5	120°	18.5	13.8	57.5	28.7
H_2SO_4	135°	85.9	23.0	62.2	12.5
H_2SO_4	180°	92.5	28.2	56.4	14.6
$H_2S_2O_7$	120°	97.9	27.4	58.5	14.1
$H_2S_2O_7$	95°	97.9	25.9	58.8	15.3

These results show that from the standpoint of crude yield and purity of product, fuming sulfuric acid is the best condensing agent, concentrated sulfuric acid, and phosphorus pentoxide following in the order named. The last gives a relatively higher percentage of the γ-phthalein, and if it could be used in such a manner as to give a good yield without the production of tar, it would be the most desirable condensing agent to use for the preparation of the γ-compound. Glacial phosphoric acid is very nearly worthless; evidently the statement of R. and H. Meyer in regard to the use of this substance is a typographical error. Zinc chloride, if used, must be employed for a longer period than two hours or at a higher temperature than 120°.

A critical study of the methods of isolating the isomers was also made. After a large number of experiments, testing the methods described in the literature for the separation of such isomers, and also such methods and modifications as seemed most promising, a fairly satisfactory method was developed. At the outset it was found that some of the methods used by Meyer in separating the phthaleins were slow, or gave incomplete separation, or both, and had to be modified or abandoned. For instance, the method he used for extracting the γ-phthalein (see p. 1207) was found to be unsatisfactory because (1) not all of the γ-phthalein was removed from the crude product, and (2) some β-phthalein was always carried through into the ammoniacal filtrate, which upon standing for some time was precipitated as a colloidal mass that could not be removed by filtration. This difficulty had been previously noted by Acker[1] and the method was abandoned by him. Meyer's separation of the γ- and β-isomers was therefore incomplete.

Even less complete was Meyer's separation of the α- and β-compounds. He extracted the residue obtained after removal of the γ-phthalein by means of cold soda solution or with dilute ammonia until the washings were blue-red instead of the cherry-red color first obtained. A critical examination of this method showed that it was unsatisfactory for two reasons; first, the β-phthalein was very slowly removed, and so large a number of extractions were necessary that the method was laborious, the more so as

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[1] Diplom-Arbeit, Chemie-Schule in Mülhausen i/E, 1910.

with each extraction with soda the solutions became more and more difficult to filter, due to the fact that the tarry material gradually became gelatinous under the influence of the alkali; and secondly, not inconsiderable amounts of α-phthalein were carried into the soda solution.

The method of Kehrmann for separating the γ- from traces of the β-isomer gave better results than that employed by Meyer. As mentioned above (see p. 1211) Kehrmann dissolved the crude material in methyl alcohol and passed in hydrochloric acid gas, keeping the solution at 0°, whereupon the γ-hydrochloride separated in the pure state. The last traces of the γ-compound were removed from the β-phthalein by dissolving the latter in alcohol, adding a few drops of ammonia, heating to boiling, and adding hot water until the solution became turbid. On cooling the pure β-compound crystallized out (see p. 1210). It remained then to develope a method for separating the α- from the β-compound. To accomplish this, advantage was taken of the difference in behavior of an ethereal solution of these isomers toward dilute soda solution. Meyer states that the soda solution of the α-isomer is decolorized on shaking with ether, or remains only pale bluish red. Baeyer states, however, that the soda solution of the α-compound is completely decolorized by shaking with ether. The latter statement was found to be more nearly correct, although if an ethereal solution of the α-phthalein be shaken with soda solution some color is imparted to the latter, unless the ethereal solution be quite dilute. Meyer states that the soda solution of the β-phthalein is not decolorized by ether. While this is true, a large part of the phthalein does go into the ethereal layer. On the other hand an ethereal solution of the β-isomer gives up part of its phthalein to sodium carbonate solutions, and by successively removing the latter all the β-compound can be removed from the ether.

To separate the α- from the β-isomer, the mixture of the freshly precipitated phthaleins is dissolved in ether. This ethereal solution is *filtered* and then shaken with normal sodium carbonate solution when some of the β- and a much smaller amount of the α-phthalein goes into the soda solution. This latter solution is now removed and shaken with a small portion of *fresh* ether which removes *all* the α- and a little of the β-phthalein, leaving only the β-isomer in the soda solution. After removing the sodium carbonate solution from the original ether solution, it is again extracted with fresh soda solution, the latter drawn off and shaken with the *same smaller portion of ether* that was used to extract the first soda solution. This process of extraction is repeated until a fresh portion of the soda solution when shaken with the original ether solution is only faintly colored, and this color is at once removed when the soda solution is shaken with the smaller portion of ether. The α-phthalein is now found in the ether solutions while the several soda solutions will contain only the β-compound.

For a 50 g. portion of the crude orcinolphthaleins two liters of ether in a four liter separatory funnel are used for the main ethereal solution. The smaller portion of ether is usually about 500 cc. while the portions of normal soda solution used for extraction are usually about 300 to 500 cc.

Another very important step in the purification was the removal of tarry material from the crude product. To do this advantage was taken of the very great solubility of the freshly precipitated phthaleins in ether, and of the relative insolubility of the tar in this solvent.

The method used in separating and purifying the three isomers was as follows: The cold filtered alkaline solution of the crude product is precipitated by pouring slowly into a large volume of dilute *mineral* acid (acetic acid is not suitable here because on subsequent shaking with ether it is taken up by the latter to some extent, and reduces the solubility of the phthaleins in this solvent). The mixture of the freshly precipitated phthaleins and water is shaken up in a large separatory funnel with a large amount of ether, allowed to stand until the two layers have sharply separated, when the tarry by-products collect in a flocculent dark-colored mass between the two layers. The aqueous layer is then removed, and the ether filtered (first through muslin and then through filter paper). The clear ether solution is now shaken with about one-third of its volume of normal soda solution, the two layers allowed to separate, and the aqueous one removed. This contains all the γ- except traces, considerable β-, and some of the α-phthalein. The last and most of the β-compound are removed by shaking the soda solution with fresh portions of ether, and the α- and β-phthaleins are separated as outlined above. The γ-phthalein and a little of the β-product remaining in the soda solution are recovered by acidification and the γ-isomer purified by the hydrogen chloride method of Kehrmann. For final purification of the β-phthalein, the alcoholic ammonia method of Kehrmann is used.

α-Orcinolphthalein.

Compound with Methyl Alcohol.—The crude α-orcinolphthalein obtained by the method of separation outlined above is quite pure, and when precipitated from its alkaline solution by acetic or a mineral acid, it separates in the form of *pure white* flocks. It can be crystallized quite readily from methyl or ethyl alcohol, or from glacial acetic acid. As a rule the material for experimental work was crystallized from methyl alcohol, then from glacial acetic acid, and finally from dilute warm solutions in methyl and in ethyl alcohols by the addition of water. In the latter cases, that is, when water was added to the dilute solution in either of the alcohols, perfectly white, nearly rectangular plates were obtained. The pure white material from the methyl alcohol solution was analyzed:

Subst. (I) 0.1186, (II) 0.2430; loss, (I) 0.0098, (II) 0.0195. Calc. for $C_{22}H_{18}O_5$.-CH_3OH: 8.17; found: (I) 8.26, (II) 8.02.

Sample I had been dried in the air for about 20 hours. It lost all its alcohol in one-half hour at 110°, and nothing condensed on the cool part of the tube,[1] *i. e.*, it contained no water. It lost no further weight on heating to 180°. Sample II was dried in the air for about 10 days and then heated in the electric drying apparatus[2] for one-half hour at 185°. Hence α-orcinolphthalein crystallizes from methyl alcohol with a molecule of methyl alcohol.

The residue obtained in determination II was analyzed.

Subst., 0.1003; CO_2, 0.2691; H_2O, 0.0409. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.17; H, 4.57.

α-Orcinolphthalein is insoluble in water, but easily soluble in dilute caustic alkalies with a beautiful purplish red color, the alkaline salts possessing a high tinctorial power. It dissolves with difficulty in aqueous ammonia, and in solutions of the alkaline carbonates it dissolves only on warming. The solutions in these weak alkalies are *wine-red*, not *purplish red*. Dry ammonia gas and dry hydrochloric acid gas do not act on the α-phthalein. In the more concentrated (50%) solutions of the caustic alkalies it dissolves with a pure *blue* color. From all alkaline solutions the free phthalein is thrown down on the addition of acids as white flocks. It is quite soluble in methyl and ethyl alcohols and in glacial acetic acid, and is very soluble in acetone. It is insoluble in benzene. When perfectly pure it dissolves in an alcoholic solution of ammonia *without color*. When this solution is diluted with water it becomes *reddish violet* and after a time the α-phthalein crystallizes out and the solution becomes *colorless*. The slightest trace of β- or γ-phthalein can thus be detected in the α-phthalein (see pp. 1228 and 1234).

Compound of α-Orcinolphthalein with Ethyl Alcohol.—α-Phthalein, shown to be pure by the above analysis, was dissolved in hot absolute alcohol, and the solution then allowed to cool. The fine crystals which separated during the cooling were filtered off, and the mother liquor allowed to stand two days longer. Large, well formed, colorless prisms slowly formed. These were filtered off, and water added to the mother liquor. Minute colorless crystals separated, which under the microscope were seen to possess the same form as the large ones. A sample of each crop when heated at 170° came to constant weight in one-half hour, and during the heating no moisture condensed on the cool part of the tube. The following results were obtained:

Subst., (I) 0.4793, (II) 0.4871; loss (I) 0.0545, (II) 0.0526. Calc. for $C_{22}H_{16}O_6.C_2H_5OH$: 11.34; found: (I) 11.37, (II) 10.80.

Determination I was on the phthalein crystallized from absolute alcohol on long standing, while II was on the material obtained by addition of

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[1] *Am. Chem. J.*, 41, 404 (1909).

[2] THIS JOURNAL, 32, 635 (1910); *Am. Chem. J.*, 48, 477 (1912).

water to the mother liquor. The phthalein therefore crystallizes with one molecule of ethyl alcohol.

Compound of α-Orcinolphthalein with Acetic Acid.—Some of the pure α-phthalein was dissolved in boiling glacial acetic acid, and the hot solution quickly filtered. On cooling a large crop of white, well formed, stout needles separated. These were filtered off and allowed to stand in the air for two days, when all odor of acetic acid had disappeared. A portion was then finely ground and analyzed.

Subst., 0.4069; loss, 0.0653. Calc. for $C_{22}H_{16}O_5.CH_3COOH$: 14.29; found: loss 16.05.

The sample came to constant weight when heated for one hour at 175°. In order to determine the acetic acid actually present, a weighed amount of the sample was boiled with distilled water and after filtration the free acid in the solution was titrated with standard alkali using phenoltetrachlorophthalein as the indicator.

Subst., (I) 0.7844, (II) 1.1930, (III) 0.6985; 0.1 *N* NaOH, (I) 20.57, (II) 30.00, (III) 14.67 cc. Calc. for $C_{22}H_{16}O_5.CH_3COOH$: 14.29; found: (I) 15.74, (II) 15.10, (III) 12.61.

Sample I was analyzed immediately after grinding, II, 5 hours, and III, 72 hours after grinding. The phthalein therefore crystallizes with a molecule of acetic acid.

α-Orcinolphthalein Diacetate.—Fifteen grams of pure α-phthalein were boiled for one hour with an equal weight of anhydrous sodium acetate and seven times its weight of acetic anhydride. When the material was poured into cold water it separated as a colorless oil. After this had solidified, the supernatant liquid was decanted and the solid material triturated with cold normal sodium hydroxide solution, filtered off, washed and dried. It was first crystallized from absolute alcohol, from which solvent it separated in perfectly white, well-formed, stout prisms. In the melting point tube the material shrinks markedly above 230°, and finally melts sharply at 246–247°, incipient decomposition being indicated at slightly higher temperatures by the production of a greenish color. Recrystallized from ethyl acetate it formed the same type of crystals, which behaved in the same manner in a melting point tube, and melted sharply at 246–247°. It was finally crystallized from benzene and gave a melting point of 246–247°. A sample of this material heated for one-half hour at 180°, lost 2.78% (benzene of crystallization). The material left was then analyzed.

Subst., 0.1404; CO_2, 0.3627; H_2O, 0.0594. Calc. for $C_{22}H_{14}O_5(COCH_3)_2$: C, 70.25; H, 4.54; found: C, 70.45; H, 4.73.

α-Orcinolphthalein diacetate is insoluble in water, and in the alkalies, soluble in benzene and rather sparingly soluble in alcohol, and in ethyl acetate. It is readily saponified by alcoholic potash.

α-Orcinolphthalein Dibenzoate.—Five grams of pure α-phthalein were dissolved in dilute alkali in a bottle, 10 g. benzoyl chloride added, the bottle stoppered and the contents shaken vigorously for some time. Benzoyl chloride and strong alkali were added from time to time as necessary, and the shaking continued till the mixture was only slightly violet colored. The slightly yellowish, somewhat oily product was stirred up with soda solution, filtered and allowed to dry in the air. It crystallized from hot benzene in fine, white needles which melted at 276°. Recrystallized from absolute alcohol it melted at 277°. The melting point is not changed by recrystallizing from benzene. Meyer gives the melting point of this derivative as 284°. For analysis a sample was heated to constant weight at 180° for one-half hour.

Subst., 0.1060; CO_2, 0.2958; H_2O, 0.0435. Calc. for $C_{22}H_{14}O_5(COC_6H_5)_2$: C, 76.03; H, 4.26; found: C, 76.11; H, 4.59.

The dibenzoate is insoluble in water and in alkalies. Aqueous alkalies do not saponify it perceptibly in the cold, and only with difficulty on warming; alcoholic potash acts more rapidly, but still more slowly than it does on the diacetate. The dibenzoate is soluble in hot benzene, and in hot acetone, and rather difficultly soluble in hot absolute alcohol.

Tetrabromo-α-orcinolphthalein.—To 10 g. of pure α-phthalein in 125 cc. of glacial acetic acid 22 g. of bromine in 50 cc. glacial acetic acid were added dropwise with constant shaking. After standing over night the pale yellow powder was filtered off and extracted with boiling absolute alcohol. The air dried material weighed 17 g., corresponding to a yield of 90%. Five grams of this material were used in preparing the acetyl derivative (see p. 1221), and the rest dissolved in alkali by heating to boiling, filtered and precipitated by pouring into dilute hydrochloric acid. The tetrabromo compound separated as slightly colored gelatinous flocks, which on heating became very nearly white. Filtered, dried, and extracted with boiling alcohol the material was obtained as a colorless powder. The compound thus prepared agrees with the description of tetrabromo-α-orcinolphthalein prepared by Meyer (see p. 1207). It dissolves only partly in cold alkali, and on cooling the hot alkaline solution a dark-colored product slowly separates. A portion of the amorphous material was heated to constant weight at 180° and analyzed.

Subst., (I) 0.4048, (II) 0.5122; 0.1 *N* $AgNO_3$, (I) 21.41, (II) 27.08 cc. Calc. for $C_{22}H_{12}O_5Br_4$: Br, 47.31; for $C_{22}H_{13}O_6Br_3$: Br, 39.12; for $C_{22}H_{13}O_5Br_3$: Br, 40.17; found: Br, (I) 42.27, (II) 42.25.

The compound therefore loses bromine, in the alkaline solution, since the diacetate (see p. 1221) prepared from the same tetrabromo-α-orcinolphthalein analyzed in agreement with the theory. It evidently loses bromine quite easily, since the alkali used was only a little stronger than normal. The preparation was repeated.

The pale yellow powder was seen under the microscope to consist of well formed rectangular prisms. These were extracted with 200 cc. of boiling benzene which removed nearly all the color, and then with acetone, whereupon a *perfectly white product* was obtained. A sample was heated to constant weight at 180° and analyzed.

Subst., 0.3765; 0.1 *N* $AgNO_3$, 22.17 cc. Calc. for $C_{22}H_{12}O_5Br_4$: Br, 47.31; found: Br, 47.06.

This compound differs from the one previously described, and also from the one described by Meyer, in that it dissolves with difficulty in cold aqueous alkalies with a *pure blue* color, no violet being perceptible. On warming, more of the material goes into solution and the color becomes an intense pure blue; on cooling the color gradually fades, but does not become violet, and a white crystalline substance separates, presumably a salt of the tetrabromo-α-orcinolphthaleincarbinolcarboxylic acid (see pp. 1222 and 1227).

The tetrabromo compound is acted on by dry ammonia gas forming a very pale blue *di*-ammonium salt.[1]

Subst. (dried at 140°), 0.6160; gain in weight: 0.0318. Calc. for $C_{22}H_{12}O_5Br_4.2NH_3$: 4.80; found: NH_3, 4.90.

The salt is unstable, however. and loses its ammonia very quickly in the air, more quickly indeed than is the case with the corresponding β-compound (see p. 1232).

Tetrabromo-α-orcinolphthalein Diacetate.—Five grams of tetrabromo-α-orcinolphthalein were boiled with 5 g. of sodium acetate and 50 cc. of acetic anhydride for one hour, and the mixture poured into a large volume of water. The slightly colored oil was allowed to solidify, filtered off, washed, dried, and dissolved in hot benzene. The solution was concentrated by distillation, and on cooling microscopic, irregular prisms separated. The colorless compound thus prepared melted at 297° with slight decomposition. Upon recrystallization from acetone the melting point was unchanged. A sample heated to constant weight at 180° was analyzed.

Subst., 0.5111; 0.1 *N* $AgNO_3$, 27.00 cc. Calc. for $C_{22}H_{10}O_5Br_4(CH_3CO)_2$: Br, 42.07; found: Br, 42.22.

Tetrabromo-α-orcinolphthalein diacetate is insoluble in water and in alkalies. It is soluble in hot benzene, difficultly soluble in hot acetone, and almost insoluble in methyl and in ethyl alcohol.

α-Orcinolphthalein Hydrochloride.—Five grams of pure α-phthalein were dissolved in 100 cc. of absolute alcohol, the solution cooled to 0°, and treated with dry hydrochloric acid gas for two hours. A small crop of dark reddish crystals separated, which increased considerably on allowing the solution to stand over night at 0°. The dark red product was filtered off and allowed to stand in the air till the odor of hydrochloric

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[1] This work was done by Mr. J. J. Kennedy.

acid had disappeared. Examined under the microscope the material was seen to consist of well formed needles. A portion was finely ground and the loss on heating determined. The material lost weight slowly at 95°, more rapidly at 140°, finally coming to constant weight in three-quarters of an hour at 178°. It slowly became *colorless* as it lost weight.

Subst., 0.3055; loss, 0.0343. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: loss, 11.23.

The hydrochloric acid actually combined was determined by weighing a portion of the air-dried material into an Erlenmeyer flask, adding water and warming till the solution was decolorized, *i. e.*, the hydrochloride was completely decomposed. The insoluble phthalein was filtered off, washed and the free acid in the filtrate determined by titration with standard alkali using phenoltetrachlorophthalein as the indicator. From the above loss in weight the weight of the phthalein actually taken was calculated.

Hydrochloride, 0.6346; phthalein, 0.5633; HCl, 0.05762. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: HCl, 9.28.

Therefore, one molecule of α-orcinolphthalein combines with one molecule of hydrogen chloride. Probably a small amount of alcohol was present in this compound as indicated by the figure for the loss on heating. The hydrochloride is quite stable as shown by the fact that a fairly high temperature is required to drive off the hydrochloric acid.

Dry hydrochloric acid gas is without action on the α-phthalein, but when treated with fuming hydrochloric acid the *white* phthalein forms the dark red hydrochloride without dissolving in the acid.

Colorless Monopotassium Salt of α-Orcinolphthalein Carbinol Carboxylic Acid.

This salt was first prepared by A. von Baeyer (see p. 1208). According to him, it forms so readily that it may be employed as a means of separating the α- and β-isomers. The lactoid formula, which he gives to this salt to explain its lack of color, is very unusual and the compound was therefore again prepared and carefully studied.

Several preparations were made, of which the following may be taken as typical: Very pure α-phthalein, was dissolved in absolute ethyl alcohol. To this colorless solution half normal alcoholic potassium hydroxide was added slowly from a buret with constant shaking. A purplish red coloration appeared, which very quickly disappeared at first, but more slowly as the end point was approached, and meanwhile a white crystalline powder separated. The addition of alkali was discontinued before a permanent color was imparted to the solution. The potassium salt was then filtered off. It was pure white but on drying in the air for some time assumed a faint lavender tint. Dried for one-half hour at 120° in a current of hydrogen the material reached constant weight and became *markedly colored dark bluish wine-red* (it became brownish as a result of oxidation if not heated in an inert gas). The hydrogen and escaping vapors were bubbled through cold water contained in a U-tube. The contents of this tube gave a faint but distinct test for alcohol. The loss in weight (I) is due to water and some alcohol. On standing in the air all the alcohol is lost and the loss in weight from the lavender compound corresponds to one molecule of water. On heating moisture collected on the cool part of the tube of the drying apparatus, and the water through which the escaping vapors were passed gave no test for alcohol (II).

Subst., (I) 0.2804, (II) 0.3731; loss, H_2O, (I) 0.0224, (II) 0.0166.
Calc. for $C_{22}H_{17}O_6K.H_2O$: 4.33; found: H_2O, (I) 7.99, (II) 4.45.

Material dried for this short time is hygroscopic, and on *absorption of moisture becomes again nearly colorless.* If the dried *red salt* be heated for an hour and a half at 120° in a current of hydrogen it increases in weight a trifle over the weight obtained on heating for one-half hour at 120°, becomes slightly brownish, but is no longer hygroscopic, and does not lose its color on standing in the air for several days.

Potassium determinations were made in the following manner: a weighed amount of the *dried* sample was warmed in aqueous solution with an excess of 0.1 *N* hydrochloric acid until the salt was entirely decomposed. After filtering and washing the precipitated phthalein, the excess of acid remaining was determined by titration with standard alkali using phenoltetrachlorophthalein as the indicator.

Subst., (I) 0.3532, (II) 0.3218; 0.1 *N* HCl, (I) 8.86, (II) 7.95 cc.
Calc. for $C_{22}H_{15}O_5K$: K, 9.82; found: K, (I) 9.81, (II) 9.66.

Another sample of the *freshly prepared* salt was analyzed by Mr. F. W. Sherwood.

Subst., (I) 0.3639, (II) 0.4805; loss at 160°, (I) 0.1005, (II) 0.1300. Calc. for loss of 3 C_2H_5OH and 1 H_2O:[1] 28.16; found: (I) 27.62; (II) 27.06.

Both water and alcohol were given off and the salt became *colored red.* The residues were fumed down with sulfuric acid to determine the amount of potassium present.

Subst., (I) 0.2642, (II) 0.3481; K_2SO_4, (I) 0.0556, (II) 0.0755.
Calc. for $C_{22}H_{15}O_5K$: K, 9.82; found: K, (I) 9.45, (II) 9.74.

This colorless monopotassium salt of α-orcinolphthaleincarbinolcarboxylic acid dissolves with difficulty in water, imparting a wine-red color to the solution. On boiling or on long standing this dilute solution becomes colorless, and a white precipitate separates, the lactoid form of the α-orcinolphthalein.

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[1] Kober and Marshall, THIS JOURNAL, 34, 1424 (1912), have made colorless monopotassium and monosodium salts of phenolphthalein carbinolcarboxylic acid, and have found that, when made in alcoholic solutions, these salts contain both water and alcohol. In aqueous solutions these salts undergo hydrolysis and phenolphthalein precipitates exactly as this colorless salt of α-orcinolphthalein carbinolcarboxylic acid gives α-orcinolphthalein on hydrolysis.

Colored Monopotassium Salt of α-Orcinolphthalein.

Baeyer states that, if α-orcinolphthalein be boiled with soda solution, fine, hair-like needles of the violet *di*sodium salt separate out on cooling. This product was not analyzed and it was therefore deemed necessary to repeat this work, and isolate and analyze the compound. Boiling α-phthalein with normal soda solution did give on cooling a crop of hair-like needles. Under the microscope these were seen to be quite well formed and appeared wine-red by transmitted light. They formed felt-like masses on the filter and packed together so tightly that they could not be sucked dry, and as they were unstable in the presence of water or of alcohol there seemed to be no method of completely removing the mother liquor. The potassium salt prepared in an analogous manner presented similar difficulties. It was finally obtained pure as follows: Five grams of potassium carbonate dissolved in 250 cc. of 50% alcohol, were heated to boiling, and an alcoholic solution of pure α-orcinolphthalein (5 g. in 50 cc.) was added through the reflux condenser. The solution became at once purplish red colored. It was allowed to stand forty eight hours, by which time crystals had formed which were filtered off. They appeared dark red in mass and under the microscope were seen to be long, purplish red needles, almost perfectly formed. They dissolved only partly in water, and imparted a wine red color to the solution. On drying in hydrogen a sample came to constant weight in one case, I, in one hour at 110°, and in another, II, in one-half hour at 120°.

Subst., (I) 0.1379, (II) 0.1551; loss, (I) 0.0080, (II) 0.0081.
Calc. for $C_{22}H_{15}O_5K.H_2O$: 4.33; found: H_2O, (I) 5.80, (II) 5.22.

Sample I had been allowed to dry in the air for a few hours before heating, while II had stood for four days. The dried anhydrous material showed no tendency to absorb moisture and become colorless as was the case with the colorless monopotassium salt (see p. 1223). A potassium determination was made in the same manner as in the case of the colorless monopotassium salt. A portion of the dried sample, I, was used.

Subst., 0.1294; 0.1 *N* HCl, 3.34 cc. Calc. for $C_{22}H_{15}O_5K$: K, 9.82; found K, 10.09.

The following analyses were made by Mr. F. W. Sherwood on a fresh preparation of this salt:

Subst., (I) 0.1738, (II) 0.2013; loss, (I) 0.0139, (II) 0.0160.
Calc. for $C_{22}H_{15}O_5K.2H_2O$: 8.30; found: H_2O (I) 8.00, (II) 7.95.
Subst., (I) 0.1600, (II) 0.1856; K_2SO_4, (I) 0.0366, (II) 0.0422.
Calc. for $C_{22}H_{15}O_5K$: K, 9.82; found: K, (I) 10.27, (II) 10.20.

The substance is therefore a *mono-* and not a *di*-potassium salt as stated by Baeyer.

Professor Gill of the Department of Mineralogy and Crystallography of Cornell University has examined the crystals of this *red* monopotassium salt and reports as follows: "Elongated crystals or needles, which show parallel extinction and are so frequently flattened as to indicate that they are probably not tetragonal or hexagonal. Long direction less elasticity, greater absorption. Pleochroism strong, from colorless or yellowish red to purple in very thin crystals; from red with brown-orange tinge to black in the stout needles. Stout crystals with six-sided cross section. Double refraction not strong, interference color obscured by absorption in thick crystals. Optical figure symmetrical, hence not monoclinic. Without much doubt orthorhombic, possibly hexagonal, as the plane of the optical axis seems parallel to the elongation. Good cross cleavage at right angles to the length."

If this monopotassium salt of α-orcinolphthalein be boiled with a large amount of water, the wine red solution becomes decolorized, and well formed *colorless* needles of the α-phthalein separate. The solution does not become colored on cooling. If a few drops of an alcoholic solution of phenoltetrachlorophthalein be added to this colorless supernatant liquid, a marked reddish coloration results, *i. e.*, free alkali is present. The phenomenon of decoloration is, therefore, one of hydrolysis, and is in accord with the statement of Baeyer (see p. 1208) in regard to the decomposition of the colorless salt in aqueous solution and also agrees with Meyer's statement (see p. 1205) in regard to the very weak acid nature of the α-phthalein.

The ease with which this potassium salt undergoes hydrolysis in aqueous solution also explains the fact, noted by Meyer, that the solution of the α-phthalein in *dilute* potassium hydroxide is decolorized by shaking with ether. The free phthalein is very soluble in ether, but insoluble in water, and, as fast as it is formed by the hydrolysis of the salt, it is removed by the ether until finally none is present in the alkaline solution, *i. e.*, the solution is decolorized.

Dipotassium Salt of α-Orcinolphthalein.

Baeyer states that if α-orcinolphthalein be boiled with concentrated potassium hydroxide the solution becomes pure blue, and crystals of the *tetrapotassium* salt separate. He believed that the formation of this salt was due to the rupture of the pyrone ring Since the rupture of this ring is unusual, and takes place only in the case of the very acid phthaleins and since α-orcinolphthalein is a very weak acid, it was deemed necessary to repeat this work. Concentrated aqueous potassium hydroxide (1 : 1) gave a large crop of poorly crystallized material that could not be even approximately freed from its mother liquor. Analysis of this product gave over 30% potassium, the large amounts of potassium hydroxide and potassium carbonate present being indicated by slight white incrustations on the air-dried material. Anticipating this difficulty, a portion of the freshly prepared material was filtered separately, and washed several times with absolute alcohol. The filtrate was strongly purplish red colored and the material on the filter analyzed as follows:

Subst., 0.2735, dried, 0.2654; 0.1 *N* HCl, 10.83 cc. Calc. for $C_{22}H_{14}O_6K_4$: K, 29.48. Calc for $C_{22}H_{14}O_5K_2$: K, 17.92; found: K, 15.96.

The salt evidently breaks up in alcoholic solution, and the potassium hydroxide or potassium ethylate formed is washed out at a greater rate than is the free phthalein. A fairly pure salt was finally obtained as follows: seventy-five cc. of 1 : 1 potassium hydroxide were diluted to 150 cc. with water, heated to 85° and 5 g. of pure α-phthalein, dissolved in 100 cc. alcohol, added. The solution became violet, not blue colored, and on cooling two liquid layers formed. About 85 cc. of the alcohol and water were then distilled off, when the solution became pure *blue* and homogenous, and blue crystals having a bronzy luster began to separate from the hot solution. The whole was allowed to cool, whereupon the separation of the salt was nearly complete, and the mother liquor was no longer highly colored, due to the formation of the *tripotassium* salt of the carbinol acid (see p. 1227). The crystals were filtered off and dried in the air. In mass they appeared blue with a decided bronzy luster. Under the microscope they appeared pure blue. They dissolved in water almost completely at once and imparted a purplish red color to the solution. On heating in hydrogen the crystalline material came to constant weight in one-half hour at 110°.

Subst., (I) 0.4895, (II) 0.4141; loss, (I) 0.0233, (II) 0.0163.
Calc. for $C_{22}H_{14}O_5K_2.H_2O$: 3.97; found: H_2O, (I) 4.76, (II) 3.94.

Sample I had been allowed to dry over night in the air, while Sample II had stood in the air for ten days.

Potassium was determined in the same manner as in the case of the monopotassium salts.

Subst., (I) 0.4653, (II) 0.3969; 0.1 *N* HCl, (I) 21.91, (II) 19.00 cc. Calc. for $C_{22}H_{14}O_6K_4$: K, 29.48; calc. for $C_{22}H_{14}O_5K_2$: K, 17.92, found: K, (I) 18.41, (II) 18.72.

The salt is therefore a *di-* and not a *tetrapotassium* salt as stated by Baeyer (see p. 1210).

This blue dipotassium salt was obtained beautifully crystallized by dissolving 2.5 g. of the *pure* α-phthalein diacetate in 900 cc. of hot alcohol and pouring this solution into a boiling solution of 7.5 g. of potassium hydroxide in 100 cc. of alcohol. After boiling for a short time one-half of the alcohol was distilled off and the solution allowed to stand over night. The crystals were then filtered off, dried in the air. and analyzed.[1]

Subst., (I) 0.3436, (II) 0.3352; loss at 110°, (I) 0.0114. (II) 0.0111. Calc. for $C_{22}H_{14}O_5K_2.H_2O$: 3.97; found: H_2O, (I) 3.32, (II) 3.31.

This salt contained no alcohol, the loss being due entirely to water.

Subst., (dried) (I) 0.2925, (II) 0.2877, (III) 0.1408; cc. 0.1 *N* HCl, (I) 13.96, (II) 13.47, (III) 6.55. Calc. for $C_{22}H_{14}O_5K_2$: K, 17.92; found: K, (I) 18.66, (II) 18.31, (III) 18.19.

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[1] This salt was made and analyzed by Mr. F. W. Sherwood.

Professor Gill has examined the crystals of this *blue* dipotassium salt and reports as follows: "The substance is thoroughly crystalline, though not in good single crystals but in rosette-like groups of somewhat thick plates. These groups reach about $^1/_3$ mm. in diameter, and are composed of many sub-parallel individuals. There seem to be no impurities present in any appreciable quantity. The fact that extinction is in some positions parallel and in others as high as 15° or even 20° would suggest monoclinic crystallization. The surface color is a brilliant yellowish or greenish bronze. In very thin crystals the marked pleochroism is from dark purplish blue to a lighter clear blue, while thicker individuals change from black to dark blue when rotated above a nicol prism. Not enough light is transmitted to enable observation of the figure in converging polarized light." This dipotassium salt of the α-phthalein behaves, on boiling, in dilute aqueous solutions just as do the two monopotassium salts, although, of course, a proportionately larger amount of water is required to produce complete decoloration.

Tripotassium Salt of α-Orcinolphthalein Carbinol Carboxylic Acid.

This salt was obtained from the mother liquor from which the dipotassium salt had crystallized out (see p. 1226). In mass the salt appeared *pale blue* to the naked eye, but under the microscope it could be seen to consist of almost *colorless needles* mixed with some crystals of the *blue* dipotassium salt. After being dried at 155° in hydrogen the material gave results on analysis agreeing with those required for the tripotassium salt of the carbinol carboxylic acid.[1]

Subst., (I) 0.3216, (II) 0.4053; loss, (I) 0.0284, (II) 0.0347. Calc. for $C_{22}H_{15}O_6K_3.2.5H_2O$: 3.38; found: (I) 8.83, (II) 8.56. Subst., (dried) (I) 0.3584, (II) 0.2968; K_2SO_4, (I) 0.1880, (II) 0.1537. Calc. for $C_{22}H_{15}O_6K_3$: K, 23.82; found: K, (I) 23.54, (II) 23.24.

This salt undergoes hydrolysis when boiled with water, exactly as the other potassium salts of the α-phthalein do. Kober and Marshall[2] have made a *tri*potassium salt of phenolphthalein carbinolcarboxylic acid which hydrolyzes with water in the same manner that this salt does.

It is highly probable that this is the salt analyzed by Baeyer and which he called a *tetrapotassium* salt (see p. 1210).

β-Orcinolphthalein.

β-Orcinolphthalein was obtained free from its isomers as outlined above (see p. 1217). The last traces of the γ-compound were removed by the ammonia method of Kehrmann. In order to insure the complete removal of the α-isomer from the soda solution it is necessary to use *two* portions of ether, and also to take care that the concentration of the α-phthalein

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[1] These analyses were made by Mr. F. W. Sherwood.

[2] THIS JOURNAL, **33,** 1780 (1911).

in the smaller portions of ether does not become sufficiently great to permit this compound to pass into the soda solution.

The crude β-orcinolphthalein was crystallized first from methyl alcohol, then from methyl alcohol by the addition of water, and finally from ethyl alcohol by the addition of water. From the last two solutions a mixture of colorless and colored needles were obtained when the water was added to the *hot* solutions. Perfectly white needles were obtained by the addition of cold water to the solution in methyl alcohol surrounded by ice. This product was filtered off, allowed to dry in the air, and the loss on heating determined. The material came to constant weight in one hour at 120° *without becoming colored,* but on further heating for one-half hour at 185° it was converted into the stable *yellow quinoid form without change of weight.* The following determinations show that the product crystallized from methyl alcohol by the addition of water contains a molecule of methyl alcohol (I), or is a mixture of this compound with the hydrate (II), (III).

Subst., (I) 0.3640, (II) 0.5611, (III) 0.1655; loss, (I) 0.0336, (II) 0.0369, (III) 0.0117. Calc. for $C_{22}H_{16}O_5.CH_3OH$: 8.17; for $C_{22}H_{16}O_5.H_2O$: 4.76; found: (I) 9.23, (II) 6.58, (III) 7.07.

The yellow material obtained in determination (I) was shown to be the anhydrous β-orcinolphthalein (see p. 1206) by the following analysis:

Subst., 0.0920; CO_2, 0.2482; H_2O, 0.0358. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.58; H, 4.36.

The colored quinoid form of the β-orcinolphthalein was obtained crystalline in the following manner: a few grams of the material, shown to be pure by the above analysis, were dissolved in boiling alcohol, an equal volume of hot water added and the boiling continued. Yellow crystals separated, which consisted of minute, well formed, six-sided plates. The air-dried material lost only 0.1% of its weight on heating for one-half hour at 185°. From the filtrate there separated on cooling a mixture of the colored and colorless forms consisting of plates and needles, respectively. The yellow quinoid form of the β-orcinolphthalein may also be obtained crystalline from glacial acetic acid (see p. 1230).

β-Orcinolphthalein dissolves in ammonia, caustic alkalies, and in alkali carbonates with an intense cherry-red color. It does not, however, dissolve appreciably in cold ammonium carbonate, or in cold sodium bicarbonate solutions. It dissolves in alcoholic ammonia with a *red* color. When this solution is treated with water it turns *blood red.* When perfectly *pure,* and when none of the γ-phthalein is present, the solution in alcoholic ammonia shows no trace of the *greenish fluorescence* so characteristic of the γ-phthalein (see p. 1234). Dry ammonia gas does not act upon the *quinoid* form of the phthalein provided it be *perfectly pure.* Curiously enough, however, the *dry lactoid* modification absorbs nearly a molecule of dry ammonia gas (found 4.07 and 3.92% NH_3, calculated for one molecule of ammonia, 4.51%) without becoming colored. This colorless compound with ammonia loses all the ammonia when heated to 130°. When allowed to stand in the air for several weeks it loses all its ammonia and takes up moisture to form the colorless hydrate (see below).

β-Orcinolphthalein is precipitated from alkaline solutions by acetic acid as white flocks and by mineral acids as yellow flocks. The latter slowly become white on standing or at once if the mixture be heated. Kehrmann (see p. 1211) regarded this color change as one from the quinoid form of the free β-phthalein to the stable lactoid form. This is, however, incorrect, the *yellow quinoid* form being, as shown above, the *stable* one, while the *white* product is a mixture of the *unstable lactoid* and *lactoid hydrate* forms (see p. 1230). The yellow compound obtained on precipitation with mineral acids contains a small amount of the *colored* quinoid sulfate or hydrochloride, which slowly hydrolyzes in the cold, or rapidly on heating, to the colorless phthalein and its hydrate. Acetic acid does not form a salt with the phthalein, therefore it precipitates the phthalein as the *white* hydrate, which goes over to the *colored* anhydrous form on boiling (see p. 1230).

β-Orcinolphthalein Hydrate.—β-Phthalein was dissolved in dilute alkali and poured into dilute acetic acid. A white, flocculent precipitate separated, a portion of which was filtered off, washed, dried in the air, and the loss on heating determined. The material came to constant weight in one-half hour at 150°, and did not change color, but on heating for one-half hour at 185° it became *colored yellow without change of weight.*

Subst., (I) 0.2653, (II) 0.1941, (III) 0.4659; loss, (I) 0.0140, (II) 0.0100, (III) 0.0244. Calc. for $C_{22}H_{16}O_5.H_2O$: 4.76; found: H_2O, (I) 5.28, (II) 5.15, (III) 5.24.

This material had been dried in the air for two weeks. It probably contains a small amount of acetic acid (see p. 1231). Another portion of the above suspension of freshly precipitated hydrate was boiled for one hour, which caused it to change slowly from the *colorless* hydrate to the yellow phthalein. This product lost only 1.16% on heating for one-half hour at 150°. It is therefore the anhydrous quinoid form, containing a very small amount of the hydrate. This transformation was no doubt due to the solvent action which the small excess of acetic acid had on the hydrate, thus lowering decidedly the temperature of transition into the stable quinoid form. Such a transformation by partial solution is also illustrated by the following experiment. Some of the colorless air-dried hydrate was boiled in benzene for thirty minutes. It was converted into the yellow phthalein, which lost only 0.63% on heating.

That the product obtained on heating was really the anhydrous β-orcinolphthalein is shown by the following analysis:

Subst., 0.1349; CO_2, 0.3611; H_2O, 0.0558. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.00; H, 4.63.

If the β-orcinolphthalein be precipitated from alkaline solution by mineral acids it separates as a mixture of the lactoid phthalein and its colorless hydrate:

Subst., (I) 0.4246, (II) 0.2863, (III) 0.1898; loss, H_2O, (I) 0.0112, (II) 0.0070, (III) 0.0040. Calc. for $C_{22}H_{16}O_5.{}^1/_2H_2O$: 2.44; found: H_2O, (I) 2.64, (II) 2.45, (III) 2.11.

The yellow product which at first separates is completely hydrolyzed during the subsequent filtering and washing, so that the final product is perfectly white. It becomes white at once on heating the mixture, but is not further transformed into the stable quinoid form.

Behavior of β-Orcinolphthalein toward Glacial Acetic Acid.—Inasmuch as E. Fischer believed that orcinolphthalein formed a monoacetyl derivative (see p. 1202) on heating with glacial acetic acid, and further since Meyer considered this monoacetyl derivative of E. Fischer to be identical with *his* β-orcinolphthalein (see p. 1206), because the combustion analyses and certain properties of E. Fischer's product agreed with those of *his* β-orcinolphthalein, the behavior of the *pure* β-phthalein toward glacial acetic acid was carefully studied.

Some of the white β-orcinolphthalein hydrate was boiled with glacial acetic acid for some time. Only partial solution took place and the insoluble material assumed a yellow color. This material was filtered off. From the hot filtrate there separated on cooling a small crop of *yellow plates* exactly similar to those obtained from *hot* alcohol (see p. 1228). The yellow substance, *which did not dissolve in the acetic acid*, was examined under the microscope and seen to consist of needles. This material was finely ground, allowed to stand in the air until all odor of acetic acid had disappeared, and the loss in weight on heating to 125° determined.

Subst., 0.3164; loss, 0.0009 g.; loss, 0.28%.

That this dried material is the anhydrous phthalein is shown by the following analysis:

Subst., 0.1122; CO_2, 0.3015; H_2O. 0.0457. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.29; H, 4.56.

The material which separated from the *hot* filtrate in yellow plates was filtered off, dried, and analyzed. It came to constant weight in one-half hour at 190°.

Subst., 0.2351; loss, 0.0024 g.; loss, 1.02%.

The material thus dried was shown to be the anhydrous phthalein by the following analysis:

Subst., 0.0969; CO_2, 0.2599; H_2O, 0.0393. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48: found: C, 73.15; H, 4.54.

The results show that Emil Fischer's monoacetyl orcinolphthalein was probably β-orcinolphthalein containing a small amount of acetic acid (see pp. 1202 and below).

Compound of β-Orcinolphthalein with Acetic Acid.—From the cold mother liquor obtained in the preceding preparation there separated on *long standing* a small amount of perfectly white microcrystalline powder. This was filtered off, dried in the air, finely ground, and allowed to stand till the odor of acetic acid had entirely disappeared. Heated in the drying apparatus it lost considerable weight at 115°, but at the end of an hour and a half it had not come to constant weight, so the temperature was increased to 180°. In one hour it had reached constant weight, but was only slightly yellow. It assumed the *yellow* color of the quinoid β-phthalein on heating for one-half hour longer.

Subst., 0.3793; loss, 0.0569. Calc. for $C_{22}H_{16}O_5.CH_3COOH$: 14.29; found: loss, 15.00

A sample was weighed into an Erlenmeyer flask, heated with water and the filtrate from this titrated, using phenoltetrachlorophthalein as the indicator.

Subst., 0.6238; 0.1 *N* NaOH, 15.14 cc. Calc. for $C_{22}H_{16}O_5.CH_3COOH$: 14.29; found: 14.57.

The yellow material which remained after heating at 180° was pure β-phthalein.

Subst., 0.1182; CO_2, 0.3173; H_2O, 0.0466. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.21; H, 4.41.

β-Orcinolphthalein Diacetate.—β-Orcinolphthalein, free from its isomers and from tar, was converted into the acetate (see p. 1219), and this dissolved in hot benzene. On cooling clusters of *pure white* needles separated having a melting point of 226–227°. The melting point remained the same when the substance was recrystallized from absolute alcohol or from ethyl acetate. For the analysis it was heated to constant weight for one-half hour at 180°.

Subst., (I) 0.1754, (II) 0.1020; CO_2, (I) 0.4527, (II) 0.2625; H_2O, (I) 0.0732, (II) 0.0440. Calc. for $C_{22}H_{14}O_5(CH_3CO)_2$: C, 70.25; H, 4.54; found: C, (I) 70.39, (II) 70.19; H, (I) 4.67, (II) 4.83.

β-Orcinolphthalein diacetate is insoluble in water, and in the alkalies, but is easily saponified by heating in the latter. It is quite readily soluble in hot benzene, slightly less so in hot absolute alcohol. It is rather easily soluble in acetone. It corresponds closely in its properties to the compound prepared by Meyer except that he reports it as being slightly colored.

β-Orcinolphthalein Dibenzoate.—Attempts to prepare this compound by boiling the β-phthalein with benzoyl chloride gave a product insoluble in alkalies, but which contained tar that was not easily removed by crystallization. It was then prepared by the Schotten-Baumann reaction (see p. 1219), boiled with alcohol, and the white residue crystallized from benzene.

Fine, white needles were obtained which melted at 234–235°. When recrystallized from benzene by the addition of absolute alcohol, or from alcohol they melted at 235–236°. The melting point given by Meyer for this compound, 244–245°, is certainly incorrect. For analysis the compound was dried at 195°.

Subst., 0.1342; CO_2, 0.3741; H_2O, 0.0535. Calc. for $C_{22}H_{14}O_5$ $(C_6H_5CO)_2$: C, 76.03; H, 4.26; found: C, 76.03; H, 4.46.

β-Orcinolphthalein dibenzoate is insoluble in water, and in alkalies, and saponifies somewhat slowly with alkali. It is easily soluble in hot benzene, rather difficultly soluble in hot alcohol, difficultly in ethyl acetate.

Tetrabromo-β-orcinolphthalein was made from 20 g. of *pure* β-orcinolphthalein by the method given for the corresponding α-compound (see p. 1220). It weighed 35 g. which corresponds to 94.8% of the theory. Ten grams of this material were used for conversion into the diacetate, while the remainder was dissolved in cold alkali, filtered, and precipitated by pouring into dilute acid. It separated in white, gelatinous flocks, which after filtering and washing were extracted with three portions of alcohol, whereby a white amorphous powder was left. This gave the following result on analysis:

Subst., 0.5355; 0.1 *N* $AgNO_3$, 31.68 cc. Calc. for $C_{22}H_{12}O_5Br_4$: Br, 47.31; found: Br, 47.28.

This tetrabromo-β-orcinolphthalein corresponds, in the main, to the compound prepared by Meyer. It is practically insoluble in all ordinary solvents; it dissolves in alkalies with a peculiar dirty dark reddish brown color, which in large volumes appears almost black by reflected light, but appears a dirty red by transmitted light.

Action of Dry Ammonia on Tetrabromo-β-orcinolphthalein.—Gaseous ammonia dried by passing through soda-lime, and then through a tube containing sodium wire was allowed to act on a weighed amount of tetrabromo-β-orcinolphthalein dried at 185°. The ammonia acted at once on the phthalein as indicated by the marked color, although eight hours were required to reach constant weight. The salt is almost black and is unstable. For this reason it must be placed in a tightly stoppered weighing tube when removed from the apparatus and weighed at once. On standing in the open air approximately half the ammonia was lost in three-quarters of an hour, and practically all of it had disappeared at the end of two days.

Subst., 0.3847; gain, 0.0360. Calc. for $C_{22}H_{12}O_5Br_4.3NH:NH_3$, 7.03; for $C_{22}H_{12}O_5Br_4.4NH_3$: 9.16; found: NH_3, 8.56.

The statement of Meyer[1] that "Ammoniakdämpfe wirken nicht auf ihn ein, sodass er sich leicht aus einen Gemenge von Tetrabrom-β- und γ-orcinolphthalein isoliren lässt," is therefore incorrect.

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[1] *Ber.*, **29**, 2637 (1896).

Tetrabromo-β-orcinolphthalein Diacetate.—Ten grams of the tetrabromo-β-phthalein were converted into the acetate (see p. 1221). The crude product dissolved in hot benzene and crystallized by the addition of alcohol gave white needles which melted at 265–266°. Recrystallized from ethyl acetate they melted at 266–267°. A sample was dried at 180° for one-half hour and analyzed.

Subst., 0.3897; 0.1 *N* $AgNO_3$, 20.50 cc. Calc. for $C_{22}H_{10}O_5Br_4(CH_3CO)_2$: Br, 42.07; found: Br, 42.04.

Tetrabromo-β-orcinolphthalein diacetate is insoluble in alkalies; it is less readily saponified by aqueous alkali than the β-orcinolphthalein diacetate. It is quite soluble in hot benzene, rather difficultly soluble in hot ethyl acetate, and almost insoluble in hot absolute alcohol.

β-Orcinolphthalein Hydrochloride was made by the method given for the α-compound (p. 1221). The product was bright red, and under the microscope appeared as almost perfectly formed diamond-shaped plates. A small portion was finely ground and the loss on heating determined. It lost weight very slowly at 140°, but came to constant weight in one and one-half hours at 175°, gradually changing from *red* to *yellow*.

Subst., 0.3408; loss, 0.0415. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: loss, 12.18.

The amount of hydrochloric acid combined was determined by titration as in the case of the α-compound.

Subst., 0.5564; phthalein, 0.4887; HCl, 0.0499. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: HCl, 9.26.

Hence, one molecule of the phthalein combines with one molecule of hydrochloric acid. The difference between the figures obtained for the loss on heating and the hydrochloric acid actually present is probably due to a small amount of alcohol. Dry hydrochloric acid gas is without action on the β-phthalein, but the scarlet red hydrochloride is formed at once when it is treated with fuming hydrochloric acid.

γ-Orcinolphthalein.

γ-Orcinolphthalein was separated from the crude material by the method outlined above (see p. 1217). It may also be extracted from the crude product with a 10% solution of sodium bicarbonate. This dissolved the γ-isomer very slowly, however. Ammonium carbonate is a little more rapid, but has the disadvantage that traces of the β-compound are removed by it. The hydrochloric acid method of purifying the crude γ-compound proposed by Kehrmann (see p. 1211) was used in order to insure an absolutely pure product for this work. The solution in methyl alcohol was cooled to 0°, and treated with hydrochloric acid gas. The yellow-brown hydrochloride, which separated in rather poorly formed needles, was dissolved in alkali, the phthaleins precipitated with dilute acetic acid, washed and dried. This *bright yellow* material was then crystallized from methyl alcohol and again converted into the hydrochloride, which now separated as clear yellow, almost perfectly formed needles. When this salt was dissolved in alkali, and the solution poured into dilute acetic acid the hydrate of the pure phthalein separated as *white* flocks (see p. 1235). In this manner a product is obtained which is absolutely free from tar (which apparently adheres more tenaciously to this isomer than to the others) and is also free from the isomeric phthaleins.

The γ-orcinolphthalein thus purified dissolves in alkalies with a clear yellow color, showing only a faint fluorescence, whereas the crude material exhibited a marked fluorescence. In both cases the fluorescence is very much increased by the addition of alcohol. Thicker layers of the more concentrated alkaline solutions show a slightly reddish brown color. When an alkaline solution of this *carefully purified* phthalein is poured into dilute acetic acid a *white* flocculent precipitate of the hydrate is formed (see p. 1235), whereas if not pure it gives a *yellow* precipitate. The hydrate made from *pure* material becomes beautifully crystallized on boiling for a short time with water (see p. 1236), being converted into the *yellow* anhydrous phthalein.

Pure γ-orcinolphthalein has remarkably little color in alkaline solutions as compared with the α- and β-isomers. For this reason, and because of the slight fluorescence in dilute alkaline solutions, the compound was not recognized as a phthalein until an analysis had been made. It is quite probable that the γ-phthalein in alkaline solutions exists largely in the form of salts of the carbinol acid. Towards *concentrated* alkalies it conducts itself exactly as fluorescein[1] does. If a small stick of solid caustic potash be added to an alkaline solution of the phthalein and the solution be boiled, the color changes from red to bluish green. On dilution this color changes back to red and, on standing or warming, to yellow with a greenish fluorescence which shows more distinctly on the addition of alcohol.

γ-Orcinolphthalein dissolves in ammonium and alkali carbonates and bicarbonates with the evolution of carbon dioxide. It dissolves quite slowly in ammonium carbonate, and in sodium and ammonium bicarbonate solutions. In alcoholic ammonia it dissolves with a *red* color and strong *greenish fluorescence*. When diluted with water this solution turns yellow and the greenish fluorescence becomes less marked. It crystallizes well out of methyl or ethyl alcohol, and acetic acid, or by the addition of water to any of these solutions.

Compound of γ-Orcinolphthalein with Ethyl Alcohol.—Some of the pure material was dissolved in ethyl alcohol, the solution cooled, and crystallization caused to take place by the addition of water. The material separated as colorless plates, which on heating at 110° for two hours

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[1] See *Ann.*, 372, 108 (1910).

came to constant weight and became *bright golden yellow.* When heated to 185° it became *grayish white without further loss of weight.*

Subst., 0.3074; loss, 0.0352. Calc. for $C_{22}H_{16}O_5.C_2H_5OH$: C_2H_5OH, 11.34; found: C_2H_5OH, 11.45.

This loss was due entirely to alcohol; no moisture condensed on the tube.

γ-Orcinolphthalein therefore crystallizes with a molecule of ethyl alcohol. That the above material is the pure phthalein is shown by the following analysis:

Subst., 0.1139; CO_2, 0.3078; H_2O, 0.0497. Calc. for $C_{22}H_{16}O_5$: C, 73.31; H, 4.48; found: C, 73.70; H, 4.88.

The *dark orange* colored product observed by R. and H. Meyer (see p. 1207) was obtained in this work only in the case of *impure material. Crude* γ-phthalein which had been obtained from the unpurified mixture was crystallized from glacial acetic acid, whereby *dark orange* colored, rather poorly formed crystals separated. This product after drying in the air, when heated to 175° in the drying apparatus lost weight and fused to a dark, plastic mass which on cooling became hard and brittle, *i. e.*, contained tar. The carefully purified γ-phthalein when crystallized from glacial acetic acid is *yellow;* the *dark orange* colored product observed by Meyer and also in this work is therefore impure.

Compound of γ-Orcinolphthalein with Methyl Alcohol.—If a saturated solution of pure γ-phthalein in methyl alcohol be allowed to stand, colorless cubical crystals separate. These lose weight very slowly at 110°, rapidly at 160°, coming to constant weight in one-half hour. They change to a bright yellow color as they lose weight and on heating to 185° or 190° for one-half hour longer they change to a grayish white.

Subst., (I) 0.9046, (II) 0.5225, (II*a*) 0.3824, (II*b*) 0.3481; loss, (I) 0.0762, (II) 0.0434, (II*a*) 0.0316, (II*b*) 0.0288.

Calc. for $C_{22}H_{16}O_5.CH_3OH$: CH_3OH, 8.17; found: CH_3OH, (I) 8.42, (II) 8.31, (II*a*) 8.26, (II*b*) 8.27.

Determinations I and II were made on material crystallized from pure methyl alcohol, (II*a*) and (II*b*) on the white needles obtained by the addition of water to the mother liquor from which the material used in determination II had separated. The loss was entirely due to alcohol as no moisture condensed on the tube.

γ-Orcinolphthalein Hydrate.—A few grams of *pure* γ-phthalein were dissolved in sodium carbonate solution, and poured into dilute acetic acid. The *white* flocculent precipitate was filtered off, washed, dried in the air, and the loss on heating determined. All the water was given off in two hours at 70°, and moisture condensed on the cool part of the drying tube. The material gradually changed to a *bright yellow* as it lost water. It lost no further weight on being heated for one-half hour at 180°.

Subst., (I) 0.2472, (II) 0.2448, (III) 0.1907, (IV) 0.2304; loss, (I) 0.0123, (II) 0.0116, (III) 0.0093, (IV) 0.113.

Calc. for $C_{22}H_{16}O_5.H_2O$: H_2O, 4.76; found: H_2O, (I) 4.98, (II) 4.74, (III) 4.88, (IV) 4.90.

These determinations were made on three different preparations: (I), (II) and (III) were on material that had dried in the air from five to seven days, while (IV) was on material that had stood in the air for *five weeks*.

When the hydrate is boiled with water it is converted into anhydrous γ-phthalein. A portion of the above prepared hydrate was boiled with water for two hours, at the end of which time it had become *yellow* and beautifully crystallized in rhomboidal plates. This material lost only 0.01% of its weight on heating to 180° for half an hour, *i. e.*, it is the anhydrous phthalein. Another preparation of the hydrate lost 4.53% water and became *bright yellow* when kept in a Hempel vacuum desiccator for 24 hrs. with sulfuric acid.

γ-Orcinolphthalein Diacetate.—γ-Phthalein was converted into its diacetyl derivative in the same manner as in the case of the α-isomer (see p. 1219). The colorless crude product was crystallized from benzene. Perfectly white needles were obtained which melted sharply at 206–207°. When recrystallized from absolute alcohol, and then from ethyl acetate, the melting point of the substance remained the same. For analysis a sample was dried for three-quarters of an hour at 195°.

Subst., 0.1470; CO_2, 0.3782; H_2O, 0.0613. Calc. for $C_{22}H_{14}O_5(CH_3CO)_2$: C, 70.25; H, 4.54; found: C, 70.17; H, 4.67.

The diacetate corresponds exactly to the compound prepared by Meyer. It is insoluble in water and in alkalies and is easily saponified by the latter, especially if alcohol be added. It is soluble in benzene, hot absolute alcohol, and hot ethyl acetate, and crystallizes from any of these solutions.

γ-Orcinolphthalein dibenzoate was made by the method used in making the α-isomer (see p. 1219). After filtering off the slightly orange-colored product, it was triturated with alkali, washed with water, boiled with alcohol and crystallized from benzene by the addition of absolute alcohol. Pure white needles were obtained which melted at 284–285°, with slight carbonization. When recrystallized from acetone its melting point was unchanged. For analysis the material was dried for one-half hour at 190°.

Subst., 0.0825; CO_2, 0.2300; H_2O, 0.0334. Calc. for $C_{22}H_{14}O_5(C_6H_5CO)_2$: C, 76.03; H, 4.26; found: C, 76.04; H, 4.53.

The dibenzoate is insoluble in alkalies, and is saponified rather slowly by these solutions. It is easily soluble in benzene, and rather difficultly soluble in hot acetone. It is almost insoluble in methyl and ethyl alcohols and in ethyl acetate.

Tetrabromo-γ-orcinolphthalein was made in the same manner as the α-isomer (see p. 1220), dissolved in alkali, and precipitated by pouring into dilute acid. The orange-colored flocks were filtered off, washed, and then boiled with alcohol, this treatment changing the product to a colorless form. For analysis it was heated for half an hour to 175°.

Subst., 0.4616; 0.1 *N* $AgNO_3$, 27.27 cc. Calc. for $C_{22}H_{12}O_5Br_4$: Br, 47.31; found: Br, 47.22.

Tetrabromo-γ-orcinolphthalein corresponds closely with the compound prepared by Meyer. It shows the greatest analogy to eosin of any of the tetrabromoorcinolphthaleins, dissolving in alkalies with a rose-red color. It is a good dye and is almost insoluble in all the ordinary solvents.

Tetrabromo-γ-orcinolphthalein diacetate was made by the method used in preparing the α-isomer (see p. 1221). The crude product was crystallized from ethyl acetate. In the melting point tube it became pink above 240°; this color disappeared above 270°, and the slightly darkened material melted quite sharply at 282–283°, and carbonized at a slightly higher temperature. When recrystallized from absolute alcohol it was obtained as perfectly white, well formed rhomboidal plates. These behaved in a melting point tube exactly as did the above material, and also melted at 282–283°. Bromine determinations were made on the material dried at 180° for one-half hour.

Subst., (I) 0.3358; (II) 0.5090; 0.1 *N* $AgNO_3$, (I) 17.35, (II) 26.25 cc. Calc. for $C_{22}H_{10}O_5Br_4(CH_3CO)_2$: Br, 42.07; found: Br, (I) 41.30; (II) 41.23.

The only explanation of the low percentage of bromine that suggests itself is that during the acetylation a small amount of bromine was eliminated by the action of the sodium acetate, since the tetrabromo compound from which the diacetate was made gave results on analysis for bromine agreeing with the theory (see above).

The diacetate is soluble in hot benzene, moderately in hot ethyl acetate, and quite difficultly soluble in hot absolute alcohol. It is insoluble in water and in alkalies, and is saponified rather difficultly by aqueous solution of the alkalies.

Action of Dry Ammonia Gas on γ-Orcinolphthalein.

Diammonium Salt of γ-Orcinolphthalein.—That γ-orcinolphthalein is more acid than its isomers is shown by the fact that it is acted upon so readily by dry ammonia gas. When the pure dry γ-phthalein was placed in a current of dry ammonia gas it gained weight rapidly, changed color (yellow to orange) and came to constant weight in 17 minutes. The boat containing the material was placed at once in a tightly stoppered tube and weighed. The gain in weight corresponds to two molecules of ammonia. The salt formed is unstable, however, and loses its ammonia rapidly on standing in the air.

Subst., 0.3871; gain, (NH_3), 0.0377. Calc. for $C_{22}H_{14}O_5(NH_4)_2$: NH_3, 8.64; found: NH_3, 8.87.

Fluorescein and tetrachlorofluorescein[1] conduct themselves towards dry ammonia gas in the same manner as the γ-phthalein, thus showing the close resemblance of the γ-phthalein to fluorescein. The γ-phthalein is the only one of the isomers which forms a *salt* with ammonia gas.

Action of Dry Ammonia Gas on the Anhydrous Tetrabromo-γ-orcinolphthalein.—Dry ammonia gas was allowed to act on the anhydrous tetrabromo-γ-orcinolphthalein. It became pink at once, changed in a short time to a bright red, and at the end of three hours had become dark red. Approximately four molecules of ammonia are absorbed. The compound thus formed is unstable, giving up its ammonia slowly on standing in the air.

Subst., 0.5677; gain, (NH_3), 0.0551. Calc. for $C_{22}H_{12}O_5Br_4.3NH_3$: NH_3, 7.03. Calc. for $C_{22}H_{12}O_5Br_4.4NH_3$: NH_3, 9.16; found: NH_3, 8.85.

Tetrachloroeosin combines with *five* molecules of ammonia.[2]

γ-Orcinolphthalein Hydrochloride.—A portion of the γ-phthalein hydrochloride, purified as described above (see p. 1233), was dried in the air, ground, and the loss on heating determined. The compound is quite stable, losing weight slowly at 140°, and coming to constant weight only after four and one-half hours heating at 175°.

Subst., 0.4373; loss, 0.0502. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: loss, 11.48.

The amount of hydrochloric acid actually present was determined by titration in the same manner as in the case of the isomeric compounds (see pp. 1221 and 1233).

Hydrochloride, 0.3287; phthalein, 0.2910; HCl, 0.02891. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: HCl, 9.04.

The difference between the loss on heating and the amount of hydrochloric acid actually present is due to the presence of a small amount of alcohol.

Dry hydrochloric acid gas acts on the anhydrous γ-phthalein, one molecule of the acid being taken up with but little change in color. When heated to 180° the hydrochloride loses all its hydrochloric acid and gives the original weight of the γ-phthalein. The material thus obtained, when placed in a current of dry hydrochloric acid gas, again absorbs an equivalent of one molecule of hydrochloric acid, coming to constant weight in an hour and a half. The original weight of the γ-phthalein was obtained a second time by heating the hydrochloride to 180°.

Subst., (I) 0.4472, (II) 0.4472; gain in wt., (I) 0.0494, (II) 0.0452. Calc. for $C_{22}H_{16}O_5.HCl$: HCl, 9.20; found: HCl, (I) 9.95, (II) 9.18.

In (I) the boat containing the material was quickly transferred to a tightly stoppered tube, and weighed at once. In (II) the material was

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[1] THIS JOURNAL, **36**, 690 (1914).

[2] *Ibid.*, **36**, 706 (1914).

allowed to stand in the air a few minutes before being placed in the weighing bottle.

γ-Orcinolphthalein therefore combines with one molecule of hydrochloric acid *gas*. It is the only one of the three orcinolphthaleins that does this. It thus shows its great analogy to fluorescein which also combines with a molecule of hydrochloric acid gas.[1] When treated with fuming hydrochloric acid the γ-phthalein also forms the yellow hydrochloride.

Orcinoltetrachlorophthaleins.

The orcinoltetrachlorophthaleins were prepared by fusing tetrachlorophthalic acid with pure orcinol in the presence of zinc chloride, phosphorus pentoxide, concentrated sulfuric acid, or fuming sulfuric acid (containing 15% of free SO_3). The tetrachlorophthalic acid was the commercial product of Heller and Merz purified by the method of Delbridge.[2] The purity of the product used was checked by molecular weight determinations made by titrating a weighed sample with standard alkali.[3]

Subst., (I) 0.5781, (II) 0.3398; 0.1 *N* NaOH, (I) 37.03, (II) 21.72 cc. Calc. for $C_6Cl_4(COOH)_2.0.5H_2O$: mol. wt., 312.90; found: mol. wt., (I) 312.20, (II) 312.87.

Twenty grams tetrachlorophthalic acid, 19 g. orcinol, and 19 g. freshly fused zinc chloride were ground intimately, transferred to a 250 cc. round bottom flask and heated in a sulfuric acid bath to 160–170°. The reaction began at once, as indicated by the appearance of a red color, and the mixture soon formed a pasty mass which partly solidified at the end of two hours. The hard red mass was ground, dissolved in normal alkali by heating, the solution filtered, and acidified with hydrochloric acid. *Dark red flocks* separated. The mixture was then boiled with steam, and the crude orcinoltetrachlorophthaleins filtered off. The *dark red* product dried at 110° (28 g.) corresponded to a yield of 85%.

Phosphorus pentoxide was next used as the condensing agent. One hundred and fifty-six grams of tetrachlorophthalic acid, 145 g. of orcinol, and 140 g. of phosphorus pentoxide were ground together and fused as above. The contents of the flask melted to a red viscous mass which did not solidify in two hours. The mixture treated as before gave 162 g. of a *dark red* product, a yield of 65%.

The crude product obtained in these two syntheses could be separated into its isomers only with the greatest difficulty. Ether could not be satisfactorily used, as it had been in the case of the orcinolphthaleins (see p. 1216), owing to the fact that a dark red material caused the ether to form emulsions with the alkali, which were so stable that the process was slow and laborious. Sufficient amounts of the isomers were finally obtained, however, to show that this dark red material was an impurity and not a quinoid form of one of the isomers. Indeed it was found (see p. 1242) that this red material was formed by the decomposition of the β-orcinoltetrachlorophthalein itself in *hot* dilute alkaline solutions. Consequently, in the subsequent preparations the crude material was dissolved only in *cold* alkali.

Sulfuric acid was then used as the condensing agent. Fifty grams of tetrachlorophthalic acid, 48 g. of orcinol and 45 cc. concentrated sulfuric acid were heated to 135° for two hours. During the fusion the temperature rose to 150° for a short time. A

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[1] THIS JOURNAL, 36, 701 (1914).

[2] *Am. Chem. J.*, 41, 414 (1909).

[3] *Ibid.*, 41, 401 (1909).

secondary reaction set in as evidenced by the frothing of the mass, the formation of brownish tarry material, and the vigorous evolution of sulfur dioxide. This reaction almost entirely ceased, however, on lowering the temperature to 135°. At the end of two hours the melted mass was poured into water, the product filtered off and dissolved in *cold, dilute* alkali. On acidification the phthaleins separated as *light yellow* flocks. The mixture was heated to boiling with steam, the crude product filtered off and dried at 110°. Yield. 63%.

All of this product (46 g.) was separated into the isomers by the method given below and gave

Isomer.	Grams.
α	11.0
β	17.0
γ	8.0

and in addition a large amount of tar.

Fuming sulfuric acid was next used as the condensing agent. Forty-one grams of tetrachlorophthalic acid and 20 cc. of fuming sulfuric acid were placed in a flask and heated to 150° for some time. The temperature was then lowered to 135° and 38 g. orcinol added. The reaction proceeded so slowly that 20 cc. more of fuming sulfuric acid were added. The reaction then proceeded. as indicated by the red color of the mixture. At the end of the two hours the product was treated exactly as in the preceding case. A *light yellow* product was obtained, which after drying at 110° weighed 57 g. corresponding to a yield of 88%. This material yielded the following amounts of the different isomers:

Isomer.	Grams.
α	12.5
β	32.0
γ	7.5

On attempting to repeat this synthesis the temperature rose to 140° for a few moments. Instantly a vigorous secondary reaction began, accompanied by the evolution of sulfur dioxide. This reaction decreased somewhat when the temperature was lowered to 100°, but began again as soon as heat was applied. The product formed was largely tarry material. which contained only a small percentage of the phthaleins.

It seems from the results presented here that zinc chloride is the best condensing agent to use in the preparation of the orcinoltetrachlorophthaleins. The dark red decomposition products obtained from the material made with this condensing agent (see p. 1239) would probably not have been formed if it had not been dissolved in *hot* alkali.

The method used in isolating the isomeric orcinoltetrachlorophthaleins was very similar to that used in the case of the orcinolphthaleins (see p. 1217). γ-Orcinoltetrachlorophthalein is soluble in dilute solutions of the alkali carbonates and bicarbonates; β-orcinoltetrachlorophthalein is soluble in sodium carbonate solution, and is removed from its ethereal solution by aqueous solutions of this salt; α-orcinoltetrachlorophthalein is readily soluble only in solutions of potassium and sodium hydroxide and differs from α-orcinolphthalein in that it is not even *partially* removed from its ether solution by sodium carbonate solutions. The separation of the α- and β-isomers by ether and sodium carbonate is therefore complete.

The method used was as follows: The crude material was dissolved in cold normal alkali, and precipitated by pouring into dilute mineral acid. This mixture was then shaken with a large volume of ether, the aqueous layer drawn off, and the ether solution of the phthaleins filtered to remove tar. The ether solution was then shaken with one-fourth its volume of normal soda solution. This removed all the γ-compound, and a small amount of the β-isomer. The latter was extracted by shaking the soda solution with several portions of *fresh* ether. The crude γ-product obtained by acidifying this soda solution is only approximately pure, and is further purified as indicated below (see p. 1243). The ether solutions now contain the α- and β-compounds. The latter is removed by shaking with several portions of soda solution and then the former by means of sodium hydroxide solution.

α-Orcinoltetrachlorophthalein.

The major part of the α-tetrachlorophthalein obtained as outlined above was dark colored, *i. e.*, contained tarry by-products, although some portions were perfectly white. The dark colored material after being recrystallized from ethyl acetate, methyl alcohol, and ethyl alcohol, was still straw colored. It was, however, nearly pure as shown by the following analysis made on material dried at 180°:

Subst., 0.3382; 0.1 *N* $AgNO_3$, 26.95 cc. Calc. for $C_{22}H_{12}O_5Cl_4$: Cl, 28.49; found: Cl, 28.26.

This material was purified by dissolving in ethyl alcohol and precipitating with water. The air dried substance lost 7.45% of its weight on heating to 180° and some moisture condensed on the cold part of the tube. The loss calculated for one molecule of alcohol would be 8.45%. It is quite likely therefore that this compound, like the α-orcinolphthalein crystallizes with one molecule of alcohol.

An attempt was made to obtain a colorless product by saponification of the pure diacetate (see p. 1242). Fifteen grams of the diacetate were suspended in 150 cc. of absolute alcohol, an equal volume of normal sodium hydroxide solution added, and the mixture boiled for 50 minutes. The solution was then filtered, diluted and acidified with sulfuric acid. Chocolate colored flocks separated, which when filtered off, and crystallized several times from different solvents were still colored pale yellow. The filtrate obtained after saponification gave no reaction for chlorides.

Pure α-orcinoltetrachlorophthalein dissolves in alkalies with an almost *pure blue* color, having but a faint trace of red, thus differing markedly from α-orcinolphthalein. It is only slightly soluble in aqueous ammonia, and in sodium carbonate solutions. The fact that it is *not* removed from its ether solution by sodium carbonate solution while the α-orcinolphthalein is slowly extracted is unexpected, since this would seem to indicate that it unites with weak alkalies less readily than the mother substance. α-Orcinoltetrachlorophthalein is soluble in glacial acetic acid, methyl and ethyl alcohols, ethyl acetate and acetone. It is perceptibly less soluble in solvents than is the α-orcinolphthalein. When *absolutely pure* it is *colorless* and dissolves in alcoholic ammonia *without color*. The slightest trace of its isomers can thus be detected (see pp. 1243 and 1244). When water is added to this colorless solution it turns *blue* and after a few days' standing the *colorless* α-tetrachlorophthalein crystallizes out.

α-Orcinoltetrachlorophthalein Diacetate. — α-Orcinoltetrachlorophthalein was converted into the diacetate in the usual manner (see p. 1219). It was crystallized alternately from benzene and ethyl acetate until a perfectly white product was obtained which showed a constant melting point of 292°. A chlorine determination on a sample of this material dried at 180° gave the following result:

Subst., 0.3000; 0.1 *N* $AgNO_3$, 20.50 cc. Calc. for $C_{22}H_{10}O_5Cl_4(CH_3CO)_2$: Cl, 24.37; found: Cl, 24.23.

The diacetate is soluble in benzene, ethyl acetate, and acetone, and rather difficultly soluble in absolute alcohol. It crystallizes in minute, perfectly colorless rhombs. It is insoluble in water and in solutions of the alkalies, but is saponified readily on being heated in the latter. Some decomposition takes place even in the cold if alcoholic alkali be used (see p. 1241).

β-Orcinoltetrachlorophthalein.

The β-orcinoltetrachlorophthalein obtained by the method of separation described above contained a small amount of red material that imparted a faint pink tint to the product. Crystallization from methyl alcohol, ethyl alcohol, ethyl acetate and glacial acetic acid gave a product that was colorless, but on heating to 150° a faint pink tint appeared. It was shown to be pure by the following determinations made on material dried at 180°:

Subst., (I) 0.3153, (II) 0.2825, (III) 0.2830; 0.1 *N* $AgNO_3$, (I) 25.20, (II) 22.46, (III) 22.56 cc.

Calc. for $C_{22}H_{12}O_5Cl_4$: Cl, 28.49; found: Cl, (I) 28.34, (II) 28.19, (III) 28.27.

In order to determine whether this pink color was due to an impurity or to a quinoid form of β-tetrachlorophthalein, an attempt was made to obtain pure white material by the saponification of the pure β-orcinoltetrachlorophthalein diacetate (see p. 1243) with alcoholic caustic potash. The reaction began in the cold, as indicated by the production of a red color. The mixture was boiled on the water bath for one hour and filtered. A small amount of dark red, well crystallized material separated, presumably a potassium salt. The filtrate on dilution and acidification with sulfuric acid gave a precipitate of *dark red flocks, identical in properties with the dark red material* described above (see p. 1239). The filtrate from this product gave a strong reaction for chlorides. β-Orcinoltetrachlorophthalein therefore decomposes in hot alkaline solutions with the elimination of chlorine to give a substance which in the free state is dark red. The faint pink color noted in the β-orcinoltetrachlorophthalein is no doubt due to a trace of this material. The red crystalline material, presumably a potassium salt, was soluble in water, and this solution when acidified gave a red flocculent precipitate.

Pure β-orcinoltetrachlorophthalein is soluble in methyl and ethyl alcohols, acetone, glacial acetic acid, and ethyl acetate. It is soluble in alkalies with a smudgy red color intermediate between that of β-orcinolphthalein and tetrabromo-β-orcinolphthalein. From these solutions it is precipitated as a *white hydrate* by acids. A colored form of the free β-orcinoltetrachlorophthalein analogous to that obtained in the case of β-orcinolphthalein was never observed. In alcoholic ammonia it dissolves with a deep red color, but *without fluorescence*. It is thus possible to detect the presence of the slightest trace of the γ-compound (see p. 1244).

β-Orcinoltetrachlorophthalein Diacetate.—β-Orcinoltetrachlorophthalein was acetylated in the usual manner (see p. 1219). The brownish diacetate was crystallized from benzene, ethyl acetate, and ethyl alcohol until a perfectly white product was obtained, which showed the constant melting point of 239°. A chlorine determination was made on a sample dried for one-half hour at 180°.

Subst., 0.3330; 0.1 *N* $AgNO_3$, 22.73 cc.

Calc. for $C_{22}H_{10}O_5Cl_4(CH_3CO)_2$: Cl, 24.37; found: Cl, 24.20.

The diacetate is soluble in benzene, ethyl acetate, acetone, and rather difficultly soluble in absolute alcohol. It is insoluble in water, and in alkalies. Like the isomeric α-compound it undergoes decomposition when boiled with alcoholic potash (see p. 1242).

γ-Orcinoltetrachlorophthalein.

The crude γ-orcinoltetrachlorophthalein obtained from the ether solution of the mixture of the isomers (see p. 1241) by the first extraction with soda solution was quite impure, containing sufficient of the dark red material to prevent crystallization. It was converted into its diacetate, which was more readily purified, and the pure diacetate (see p. 1244) saponified with half normal alcoholic potassium hydroxide. The solution was filtered, diluted and acidified. Perfectly white flocks separated which crystallized from methyl alcohol by the addition of water in fine, white needle clusters. After drying in the air, a sample heated to 180° for one-half hour came to constant weight without change of color and moisture condensed on the cool part of the tube.

Subst., (I) 0.4672, (II) 0.2484; loss, (I) 0.0310, (II) 0.0165.

Calc. for $C_{22}H_{10}O_5Cl_4.2H_2O$: H_2O, 6. 88.

Calc. for $C_{22}H_{10}O_5Cl_4.CH_3OH$: CH_3OH, 6.04; found: (I) 6.63, (II) 6.64.

A chlorine determination on the anhydrous material gave the following result:

Subst., 0.3234; 0.1 *N* $AgNO_3$, 25.93 cc. Calc. for $C_{22}H_{12}O_5Cl_4$: Cl, 28.49; found: Cl, 28.43.

γ-Orcinoltetrachlorophthalein possesses practically the same solubilities in the ordinary organic solvents as the α- and β-isomers. It is, however, more readily soluble in aqueous ammonia and in alkali bicarbonates than its isomers. Its dilute alkaline solutions are yellow and show a green fluorescence which is apparently greater than that of γ-orcinolphthalein. Evidence on this point was obtained by dissolving molecular equivalent quantities of the two compounds in equal amounts of tenth normal alkali and comparing the two. When dissolved in alcoholic ammonia the solution has a reddish yellow color and a marked *greenish* fluorescence.

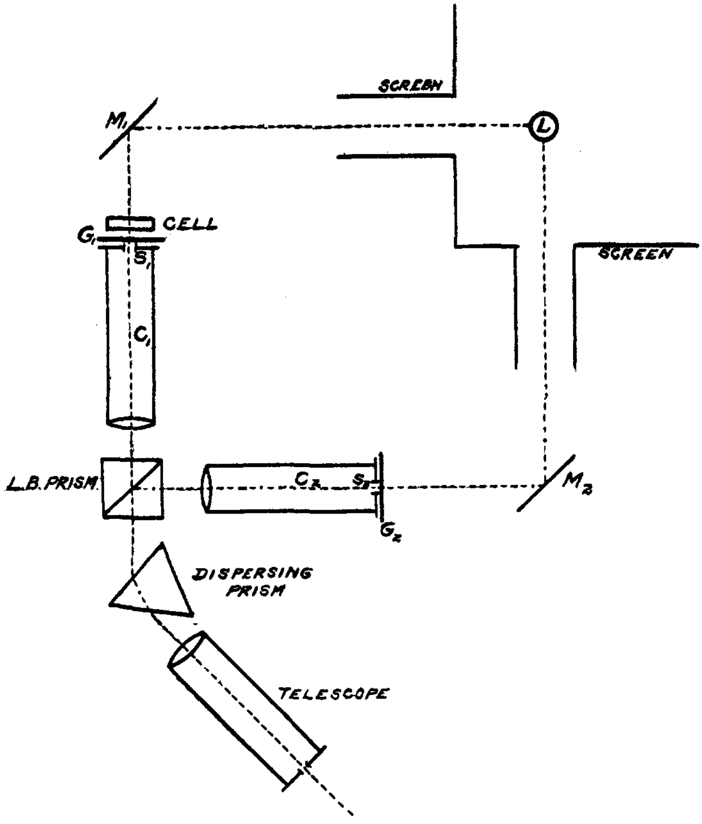
γ-Orcinoltetrachlorophthalein Diacetate.—The crude reddish brown phthalein was acetylated in the usual manner (see p. 1219). The brownish diacetate was crystallized alternately from benzene and ethyl acetate till a perfectly white compound was obtained which showed the constant melting point of 252–253°. This material dried for one-half hour at 180° was analyzed.

Subst., 0.2778; 0.1 *N* $AgNO_3$, 19.03 cc. Calc. for $C_{22}H_{10}O_5Cl_4(CH_3CO)_2$: Cl, 24.37; found: Cl, 24.29.

The diacetate is soluble in benzene, ethyl acetate, and acetone; rather difficultly soluble in absolute alcohol. From benzene it crystallizes in long, flat needles. It is insoluble in water and in alkalies, but is saponified by the latter on heating or slowly in the cold in the presence of alcohol.

Absorption Spectra of the Orcinolphthaleins, the Tetrabromoorcinolphthaleins, and the Orcinoltetrachlorophthaleins.

For absorption spectra studies weighed amounts of the pure phthaleins were dissolved in potassium hydroxide solutions of such strength that four molecules of alkali were present to each molecule of phthalein. In the case of the β- and γ-derivatives alcoholic potassium hydroxide was used, but in the case of the α-compounds aqueous alkali was used because of the tendency of these phthaleins to assume the carbinol form in the presence of alcohol. The absorption bands were studied by means of transmission curves. This work was carried out by Professor Gibbs and Mr. K. S. Gibson of the Physics Department. The following description and figures, taken from their report explain the methods used and the results obtained: "The observations were made by means of a Lummer-Brodhun spectrophotometer (see p. 1245). Light from the acetylene flame *L*, was reflected into the collimators C_1 and C_2 by mirrors, M_1 and M_2. Ground glass plates, G_1 and G_2, were placed in front of the slits in order to produce a uniform field. After passing through the collimators light passes through the Lummer-Brodhun prism, and is then dispersed and observed by the telescope. The liquid to be observed is placed in the cell opposite the slit S_1. The slit in the telescope and the slit S_1 were set at equal widths and kept constant, while the observations were made by varying the width of slit S_2 until the two fields were of equal intensities.



LUMMER-BRODHUN SPECTROPHOTOMETER.

Fig. 1.

On account of the large variation in the absorption of liquids, cells of various widths were used, and in some cases it was necessary to use capillary films, which was done by putting a small amount of liquid in a cell and drawing the liquid up on one side by means of a piece of glass placed at one edge. In this way, a wedge-shape film of various widths was secured. In all cases, a cover was kept on the cells in order to prevent evaporation of the alcohol, and in all cases observations made towards the end of the run checked with those made at the beginning, indicating that very little evaporation had occurred. This precaution was found very necessary either because of the evaporation of the alcohol or because of the absorption by the liquid of something from the atmosphere, possibly carbon dioxide. In the accompanying curves the percentage of transmission is computed by dividing the observation made with the cell removed, by the observation made with the cell and liquid in place, due correction having been made for reflection at the boundary of the glass and air and at the boundary of the glass and liquid, which, in the case of the capillary film, required a correction for four boundaries of glass and air and two of glass and liquid. The wave lengths of the points of minimum transmission, *i. e.*, of maximum absorption are shown in the following table:

	Wave lengths.		
	α.	β.	γ.
Orcinolphthaleins	0.528	0.536	0.498
Orcinoltetrachlorophthaleins	0.562	0.554	0.521
Tetrabromoorcinolphthaleins	0.572	0.576	0.529
Tetrabromoorcinoltetrachlorophthalein (very dilute solution)			0.555

In the study of these absorption curves it will be noticed that in every case the absorption bands are gradually shifted towards the red end of the spectrum as we pass from the orcinolphthaleins to their bromine and chlorine derivatives, just as was found to be the case in the study of the absorption spectra of fluorescein, eosin, tetrachlorofluorescein and tetrachloroeosin.[1]

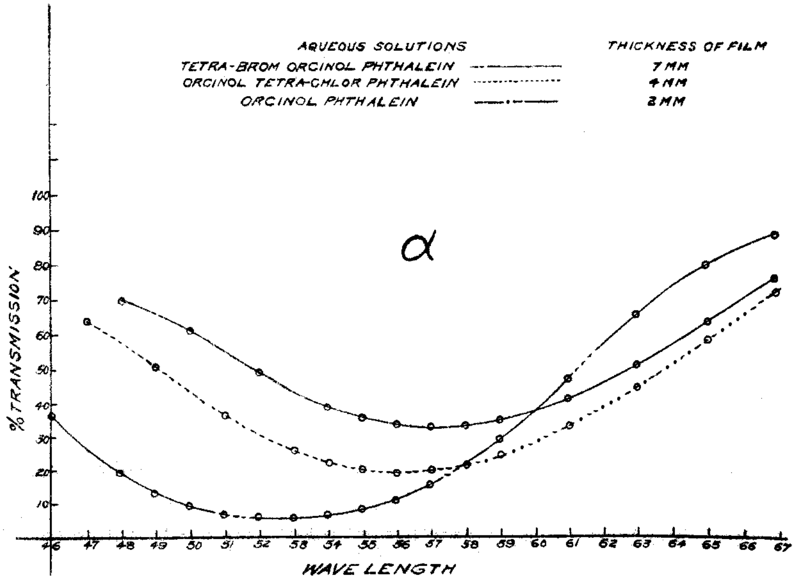


Fig. 2.

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[1] THIS JOURNAL, **36**, 680 (1914).

Again, the shifting caused by the entrance of *four* chlorine atoms into the *phthalic acid* residue of γ-orcinolphthalein is almost the same as that caused by introducing *two bromine* atoms into *each* of the two residues of orcinol, *i. e.*, the shifting is proportional to the *number of halogens*

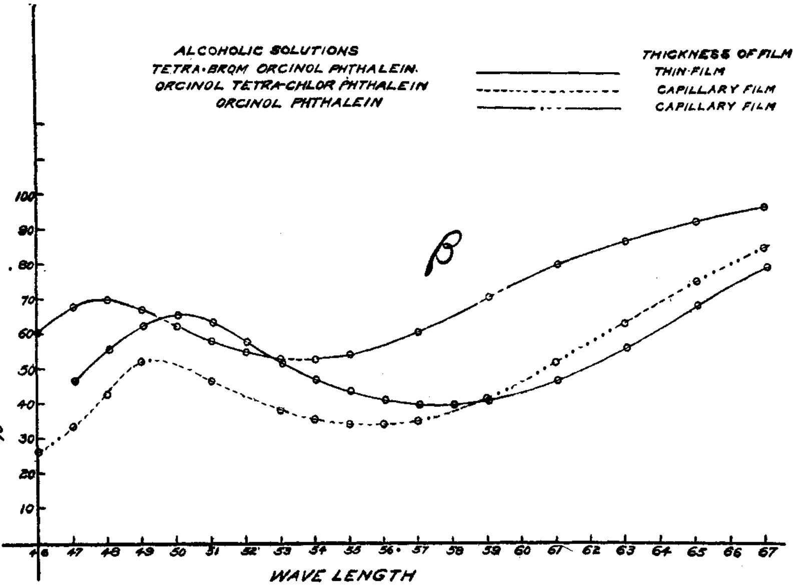


Fig. 3.

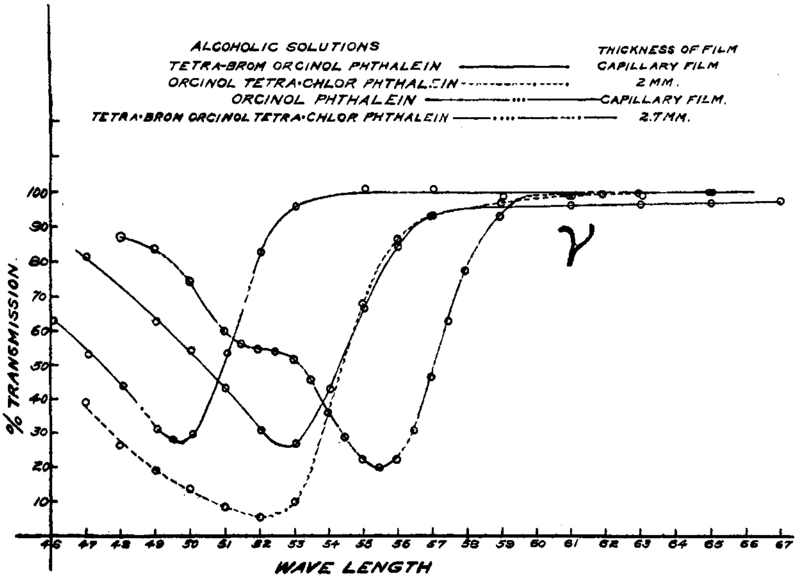


Fig. 4.

introduced, rather than to the increase in molecular weight. For example, the absorption bands of γ-orcinoltetrachlorophthalein and of tetrabromo-γ-orcinolphthalein are very nearly identical, while the molecular weights of these substances are 498 and 676.

It is interesting to note that only one absorption band is to be seen here in the case of the γ-orcinolphthalein and its halogen derivatives, while *two* were observed in the case of fluorescein and its chlorine and bromine substitution products. For this reason it seemed of importance to make the tetrabromo-γ-orcinoltetrachlorophthalein and examine its spectrum. This substance was prepared and analyzed by Mr. J. J. Kennedy. An examination of its absorption curve (see p. 1247) shows one band at 0.555 and there is evidence of another at approximately 0.520. The shape of the curves of β-orcinolphthalein and its chlorine and bromine derivatives (see p. 1247) also shows evidence of *two bands*, the second one, however, in this case being on the boundary between the visible and the ultraviolet part of the spectra.

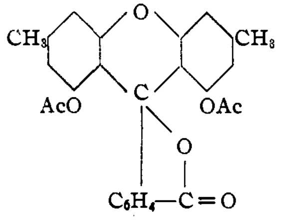
The curves for the γ-phthaleins are the typical curves found for fluorescent substances, and these phthaleins are unquestionably derivatives of fluorescein, and have, therefore a similar chemical structure.

Theoretical.

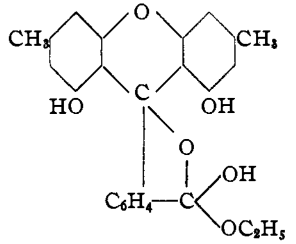
As pointed out above R. Meyer (see p. 1203) suggested Formula III for γ-orcinolphthalein, and Baeyer (see p. 1208) concluded that α-orcinolphthalein possesses the vicinal or symmetrical structure represented by Formula I. This leaves the unsymmetrical Formula II (see p. 1203) as the only one possible for the β-compound.

While there seems to be but little doubt regarding the correctness of Formula III assigned to γ-orcinolphthalein by R. Meyer, because of the marked analogy of this compound and its tetrabromo derivative to fluorescein and eosin, the evidence furnished by Baeyer (see pp. 1208 and 1210) in regard to the structure of α-orcinolphthalein is perhaps less conclusive. However, Formulas I for the α-compound and II for the β-isomer are in accord with all the known facts. According to this arrangement β-orcinolphthalein would be expected to possess properties intermediate between those of the α- and γ-isomers. In general this is the case. For example, the γ- is the strongest acid and the α-compound the weakest, while the β- is intermediate between these two. The free γ-compound exists only in the quinoid form, the β- in the lactoid and quinoid forms while the α-compound is known only in the lactoid modification. The γ-compound is the one most disposed to the formation of colored salts with acids. It evidently forms a salt even with acetic acid, as the pure material precipitated from alkaline solution by this acid is at first *colored* but on standing becomes *colorless*, just as does the compound of the β-isomer when precipitated with a *mineral acid*. In both cases this color change is probably due to hydrolysis of the colored salts of the acids. This is in accord with the fact that dry hydrochloric acid gas unites with the γ-compound while it is without action on the α- and the β-phthaleins. As pointed out by Kehrmann the β-compound is, in turn, clearly more disposed to the formation of salts with acids than is the α-compound. The nature of the absorption spectra also is in agreement with the supposition that the β-phthalein occupies a position intermediate between that of the α- and γ-isomers. It is also interesting to note that the melting point of the γ-diacetate is 207°; that of the β-compound 227°, and of the corresponding α-isomer 247°. However, as this relation does not hold in the case of the diacetates of the orcinoltetrachlorophthaleins, it perhaps should not be considered as having too much weight.

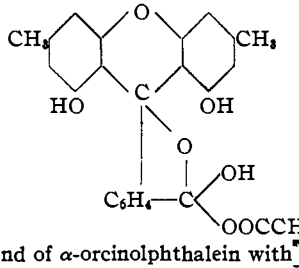
α-Orcinolphthalein, its diacetate and dibenzoate, its compound with ethyl alcohol and with acetic acid, are all colorless and hence have lactoid formulas:



α-Orcinolphthalein diacetate and dibenzoate.



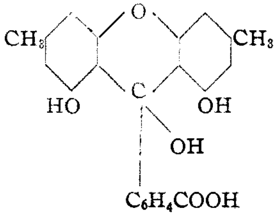
Compound of α-orcinolphthalein with ethyl alcohol.



Compound of α-orcinolphthalein with acetic acid.

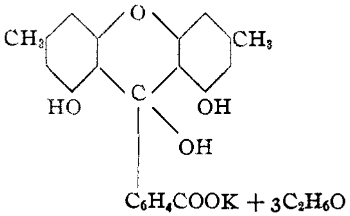
The colorless monopotassium salt formed from α-orcinolphthalein is represented as a derivative of the carbinolcarboxylic acid, Formula I (see p. 1250). As it is formed in alcoholic solution, and, when freshly prepared, loses approximately three molecules of alcohol and one of water when heated and *becomes colored,* it is represented by Formula II. On standing in the air all the alcohol is given off but not the water of constitution. Formula II without the alcohol represents this compound. Both these forms of the monopotassium salt must be considered as derivatives of the α-carbinolcarboxylic acid (I), since they are *colorless* and on heating lose water and alcohol or water alone and go over to the *colored ortho-quinoid form* (III) (see below). The lactoid formula (see p.

1209) proposed by Baeyer for this colorless monopotassium salt is not in accord with this behavior.



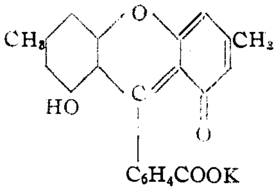
α-Orcinolphthalein carbinolcarboxylic acid, colorless.

(I).



Monopotassium salt carbinol form, colorless.

(II).



Monopotassium salt, *o*-quinoid form, colored.

(III).

The steps involved in the changes of color which α-orcinolphthalein undergoes when treated with alkalies as proposed by Baeyer are given on p. 1209.

In the light of the results obtained in this investigation, this explanation is certainly untenable because analyses show: (1) that the first violet salt is the *quinoid form* of the *monopotassium salt,* and not the *dipotassium salt;* and, (2) that the *colorless monopotassium salt* is the carbinol form of the first violet salt, and (3) that the *violet* and *blue* salts are *mono-* and *di*-potassium salts, respectively, and not *di-* and *tetra*potassium salts as stated by Baeyer.

The explanation of the color changes that is in accord with all the facts is the following: α-Orcinolphthalein is a very weak acid but forms moderately stable sodium or potassium salts. It therefore belongs to the class of pseudo acids. Such substances Hantzsch[1] considers as existing in tautomeric forms, the one practically un-ionized acid, the other considerably ionized and which gives rise to the stable salts. Applying this to α-orcinolphthalein, we have the following explanation of the color changes: The violet color first observed is due to the formation of the quinoid form of the *mono*potassium salt (III, p. 1251) by the neutralization of the true acid (II) formed from the pseudo acid (I). In alcoholic solution this color disappears because alcohol favors the conversion of the colored *mono*potassium salt (III) into the colorless salt of the carbinol

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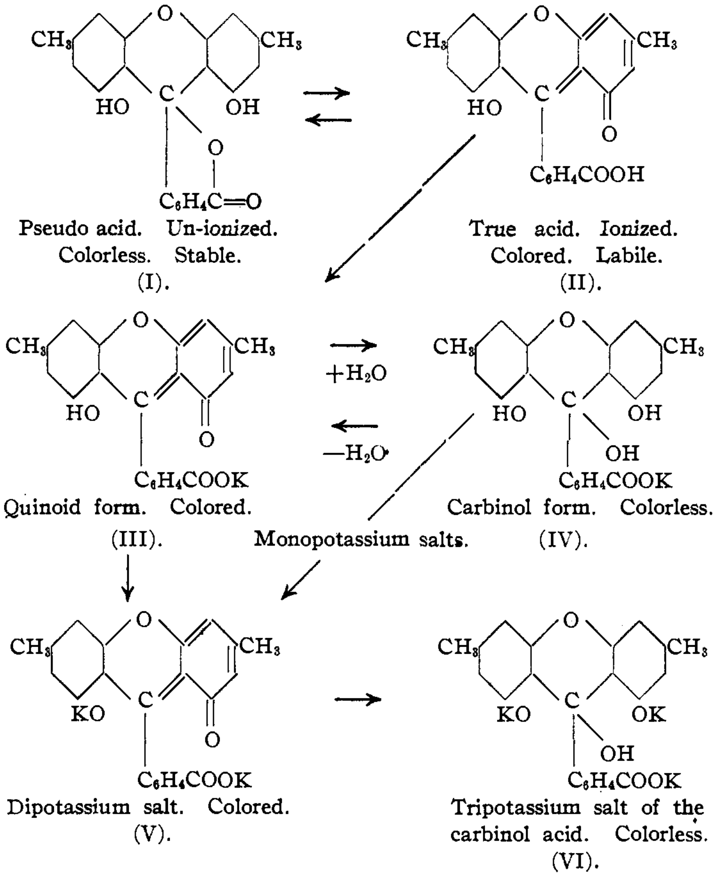
[1] *Ber.*, **32**, 575 (1899); **35**, 210, 226, 1001 (1902); **39**, 139, 1073 (1906).

acid (IV), which is practically insoluble in alcohol. On the addition of more alkali both these salts are converted into the blue *di*potassium salt (V) which, in the presence of a large excess of alkali, is converted into the colorless *tri*potassium salt of the carbinol acid (VI). On boiling with water all these salts undergo hydrolysis to alkali and the true acid (II) which then crystallizes in the form of the pseudo acid (I) which is insoluble in water.



Pseudo acid. Un-ionized.
Colorless. Stable.
(I).

True acid. Ionized.
Colored. Labile.
(II).

Quinoid form. Colored.
(III).

Monopotassium salts.

Carbinol form. Colorless.
(IV).

Dipotassium salt. Colored.
(V).

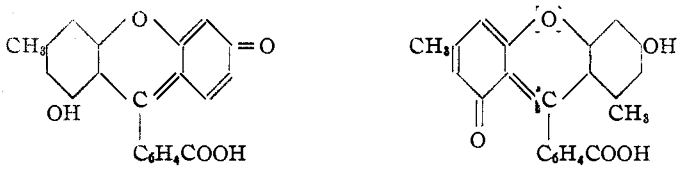
Tripotassium salt of the
carbinol acid. Colorless.
(VI).

One difference between this explanation and that of Baeyer is that in this case the potassium is represented as replacing hydrogen of the carboxyl group. Since in the true acid (II) a weak acid group (OH) and a strong acid group (COOH) exist, the stronger group would be neutralized first, *i. e.*, the first atom of potassium would replace the hydrogen of the carboxyl group. This is in agreement with the fact that the monopotassium salt is *colored* or may be readily converted into the colored form by heating. According to Baeyer, however, the potassium replaces the hydrogen of the phenol group, and the colorless salt has the lactoid structure. This structure does not agree with the fact that the colorless salt readily becomes colored on heating. This change is, however, very readily accounted for by the carbinol form assigned to the colorless monopotassium salt in the explanation given above.

Another difference between this explanation and that of Baeyer is that the pyrone ring is here represented as remaining intact. This is proved by the fact that even with a large excess of potassium hydroxide a *tripotassium* salt of the carbinol carboxylic acid (VI, p. 1251) is formed and not a *tetrapotassium* salt as represented by Baeyer (see p. 1209). A further proof that the pyrone ring is not ruptured is the fact that α-orcinolphthalein when benzoylated by the Baumann-Schotten reaction in strong alkaline solution gives a *dibenzoate* and not a *tetrabenzoate* (see pp. 1203 and 1219).

It is interesting to note that α-orcinolphthalein (see Formula I, p. 1251), in which both hydroxyl groups are *ortho* to the methane carbon atom, reacts with alkalies to form *colored* and *colorless* salts in exactly the same manner as those phthaleins in which the hydroxyl groups occupy the *para* positions to the methane carbon atom.

β-Orcinolphthalein exists in a colored modification represented by Formulas I or II.



p-Quinoid. *o*-Quinoid.

β-Orcinolphthalein. Colored.

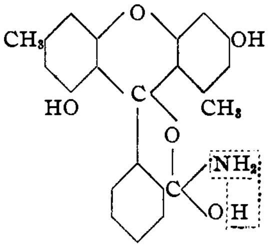
(I). (II).

and in a colorless modification represented by Formula II on p. 1203.

The lactoid modification is obtained by heating the hydrate, or the compound of β-orcinolphthalein with acetic acid, to 150°, the quinoid modification by heating the lactoid form to 180°, and by crystallizing the phthalein from *hot* alcohol or *hot* glacial acetic acid. As pointed out above (see p. 1228) it is the stable, and the lactoid the unstable form.

From the close resemblance in color of the quinoid form of the β-phthalein to that of the γ-phthalein, *which is only known in the quinoid modification*, and the fact that the *α-phthalein is only known in the lactoid form*, it seems highly probable that the *paraquinoid* formula is the one which best represents the structure of the *colored* modification of β-orcinolphthalein.

The difference in the action of dry ammonia gas on the two forms of the β-phthalein is rather surprising. From the resemblance of the quinoid form to the γ-phthalein it might have been expected that this modification of the β-phthalein would have absorbed ammonia just as the γ-isomer does, while the lactoid form bearing such a close resemblance to the α-phthalein, which is only known in the lactoid form, and which does not absorb ammonia at all, might naturally have been expected to be unacted on by this gas. Just why the lactoid form absorbs ammonia and the quinoid does not it is not possible to say, but it seems to be connected with the fact that the lactoid form gives a colorless hydrate. As the compound with ammonia has no color it may have a structure like that assigned to the hydrate (see below).

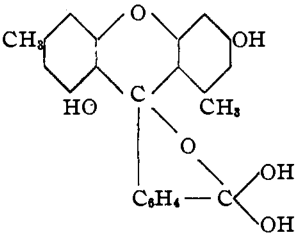


Compound of β-orcinolphthalein with ammonia.
Colorless.

This substance loses a molecule of ammonia when heated and gives the lactoid form of the phthalein, just as the hydrate does when it loses a molecule of water. Its close connection with the hydrate is also shown by the fact that it loses all its ammonia in the air and takes up moisture in its stead to form the hydrate (see p. 1229).

The statement of Fischer that orcinolphthalein forms a monacetate, and of Meyer, that the β-orcinolphthalein contains one-third of a molecule of water (see p. 1206) are both incorrect. Meyer's β-orcinolphthalein was evidently an impure product.

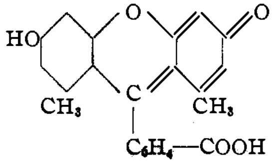
β-Orcinolphthalein hydrate is colorless and gives the colorless lactoid modification of the phthalein when heated to 150°. It is hence represented as derived from the lactoid modification:



β-Orcinolphthalein hydrate.

The diacetate, dibenzoate and the compound of β-phthalein with acetic acid are also colorless and are represented by lactoid formulas analogous to those given for the corresponding α-compounds (see p. 1249).

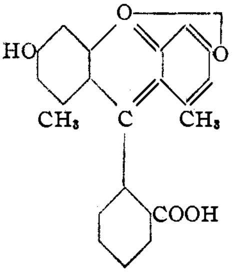
γ-Orcinolphthalein in the free condition is only known in the *colored* modification represented by the quinoid Formula I.



γ-Orcinolphthalein. Colored.

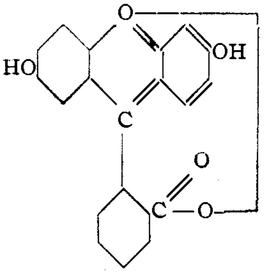
(I).

The *ortho quinoid* formula (II) assigned to this phthalein by Kehrmann is probably incorrect. If, as Kehrmann assumes, the pyrone oxygen becomes tetravalent, *i. e.*, assumes basic properties it would unite with the stronger acid group, *i. e.*, with the carboxyl. If, then, the *ortho quinoid formula* be assumed, Formula III is preferable to II.



γ-Orcinolphthalein. Ortho quinoid according to Kehrmann.

(II).

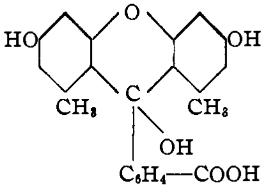


(III).

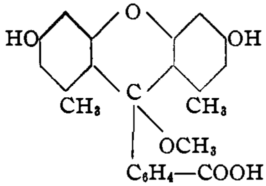
From the great resemblance of γ-orcinolphthalein to fluorescein (see pp. 1234, 1237, 1238 and 1239) it seems much more probable that both substances have the *para-quinoid* structure. From the structural formula (I) for γ-orcinolphthalein given above it will be seen that it is represented as a dimethyl fluorescein. Like fluorescein, γ-orcinolphthalein has both *acid* and *basic* properties. It unites with dry ammonia *gas* to form a *colored diammonium* salt (see p. 1238), and it is the only one of the orcinolphthaleins which acts in this way. It is also the only one of the orcinolphthaleins to combine with *dry* hydrochloric acid *gas* to form a *colored* hydrochloride. It is thus *at the same time the most acid* and the *most basic* of the orcinolphthaleins.

γ-Orcinolphthalein hydrate, the compound with methyl alcohol, the diacetate, and the dibenzoate are all colorless and hence are all derivatives of the lactoid tautomeric modification (see Formula III on p. 1203) and must therefore be assigned lactoid formulas analogous to those given for the corresponding α- and β-compounds (see pp. 1249 and 1253).

As the γ-orcinolphthalein hydrate loses water and the compound with methyl alcohol loses alcohol when heated and form the *yellow anhydrous* *phthalein,* they might be regarded as carbinol forms of this phthalein as shown below:



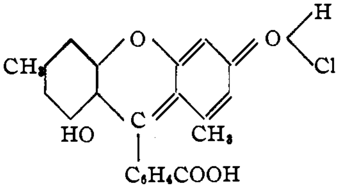
γ-Orcinolphthalein carbinol carboxylic acid. Colorless.



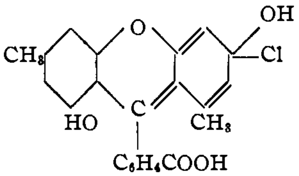
Compound of γ-orcinolphthalein with methyl alcohol. Colorless.

The ease with which the hydrate loses water (see p. 1236), however, would seem to favor the assumption that the two hydroxyl groups from which the water is formed are combined with the same carbon atom as shown in the formula given for the hydrate (see p. 1253).

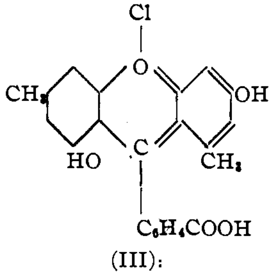
The hydrochlorides of the orcinolphthaleins are all colored and are therefore derivatives of the quinoid forms of these substances. They may be assigned the ordinary oxonium Formula I, the carbonium Formula II, or the ortho quinoid oxonium Formula III, analogous to those proposed by Kehrmann for the oxonium salts of the methylated orcinolphthaleins.[1]



(I).



(II).



(III):

β-Orcinolphthalein hydrochloride.

We may also assign the *o*-quinoid structure instead of the above *p*-quinoid (Formulas I and II) to this hydrochloride.

The hydrochlorides of the isomeric α- and γ-phthaleins may be represented by formulas analogous to the above, bearing in mind that in the case of the γ-compound only the *p*-quinoid structure can be assigned to the ordinary oxonium salt and carbonium salt, while in the case of the α-orcinolphthalein only the *o*-quinoid structure is possible.

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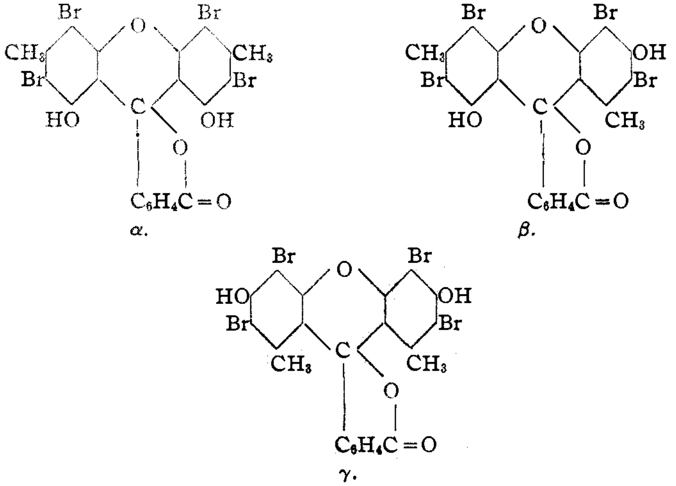
[1] *Ber.,* **45,** 3506 (1912).

In the tetrabromoorcinolphthaleins, the bromine is undoubtedly in the two orcinol residues exactly as in the case of eosin. As these compounds are all colorless they are best represented by the following lactoid formulas:

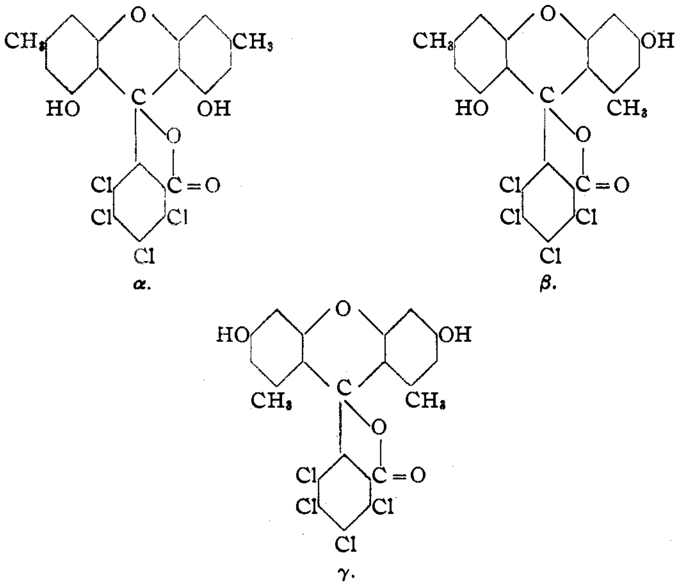


α. β. γ.

Tetrabromoorcinolphthaleins.

The colorless tetrabromoorcinolphthalein diacetates undoubtedly possess structures exactly analogous to those of the orcinolphthalein diacetates.

The orcinoltetrachlorophthaleins which are all colorless possess the structures represented by the following formulas:



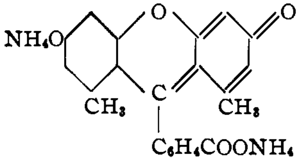
α. β. γ.

Orcinoltetrachlorophthaleins.

The formulas for the orcinoltetrachlorophthalein diacetates are derived by simple replacement of the phenol hydrogens of the above formulas by acetyl groups in each case.

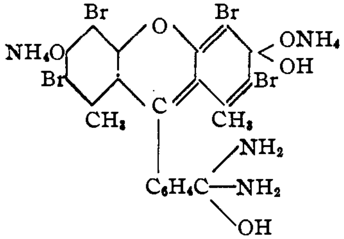
It is interesting to note that in each case in which chlorine or bromine atoms have been introduced into the phthalein molecule, the tendency to assume the free quinoid form is reduced. This is in accord with the following observation of Orndorff and Hitch. "Fluorescein in the free state exists only in the *colored* quinoid form. No colorless free fluorescein has ever been prepared. Tetrachlorofluorescein, on the other hand, has been obtained in two modifications, *colored* and *colorless*, but the colored form is the more stable. Eosin in the free state is flesh colored, and may be a mixture of the two forms, while the free tetrachloroeosin is colorless or very slightly colored. The colored modification has not yet been prepared.[1]"

In the case of γ-orcinolphthalein dry ammonia acts on this compound with the formation of a colored diammonium salt which probably has the following formula:



Diammonium salt of γ-orcinolphthalein.

In the case of the tetrabromo-β-orcinolphthalein and tetrabromo-γ-orcinolphthalein four molecules of ammonia are absorbed, which is probably best represented by such a formula as the following:



Compound of tetrabromo-γ-orcinolphthalein
with four molecules of ammonia.

The successive steps of polyammonium salt formation have been worked out by Orndorff and Hitch[2] in connection with tetrachlorofluorescein and tetrachloroeosin.

Summary.

The results obtained in this investigation may be briefly summarized as follows:

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[1] THIS JOURNAL, 36, 680 (1914).

[2] *Ibid.*, pp. 717 and 722.

1. The methods of preparing the orcinolphthaleins and of separating the isomers have been improved. The effect of conditions of preparation on the amounts of the isomers formed has also been studied.
2. The action of ammonia on γ-orcinolphthalein, on tetrabromo-β-orcinolphthalein, and on tetrabromo-γ-orcinolphthalein has been investigated.
3. The *colorless* and *colored* potassium salts of α-orcinolphthalein have been again prepared and analyzed and an explanation of the color changes of α-orcinolphthalein with alkalies more in accord with the facts than that proposed by Baeyer, has been suggested.
4. α-Orcinolphthalein exists only in the colorless form, while both colored and colorless forms of the isomeric β-compound have been prepared. The γ-phthalein is only known in the colored form. The tetrabromo-orcinolphthaleins and the orcinoltetrachlorophthaleins exist only in the colorless forms.
5. The colored compounds of the orcinolphthaleins with hydrochloric acid have been isolated and analyzed.
6. Colorless hydrates, acetyl and benzoyl derivatives, and colorless compounds of the orcinolphthaleins with solvents have also been prepared.
7. The three tetrabromoorcinolphthaleins and the three orcinoltetrachlorophthaleins and their diacetates have been made and studied.
8. The absorption spectra of the orcinolphthaleins, of the tetrabromo-orcinolphthaleins, of the orcinoltetrachlorophthaleins and of the tetrabromo-γ-orcinoltetrachlorophthaleins have been investigated and the transmission curves plotted.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

o- AND *p*-CHLOROBENZOYLACETIC ESTERS AND SOME OF THEIR DERIVATIVES.

BY LAMBERT THORP AND E. R. BRUNSKILL.

Received March 16, 1915.

The work presented in this article is a continuation of that begun by one of us upon the halogenated benzoylacetic esters,[1] and had for its object a study of the effect of negative substituents in the aromatic nucleus upon the ease of alkylation and upon the course of the saponification of the substituted benzoylacetic esters. In regard to ease of alkylation the chlorobenzoylacetic esters stand between benzoylacetic ester and its nitro derivatives, a condition of affairs which might be expected *a priori* from other well-known instances of the effect of a substitution of a nitro group for a chlorine atom, such as the relative instability of chloroacetic and nitroacetic acids with respect to the loss of carbon dioxide, the difference

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[1] THIS JOURNAL, **35**, 270 (1913).