

tarry mass. When the water bath was replaced by a metal bath, a few drops of liquid which smelled strongly of an isocyanate were obtained. By treating the distillate with aniline, a crystalline product, phenylbenzylurea, melting at  $167^{\circ}$  to  $168^{\circ}$ , resulted.

#### Summary.

1.  $\beta$ -Benzylformhydroxamic acid was obtained by the action of  $\beta$ -benzylhydroxylamine on formic ethyl ester.
2.  $\beta$ -Benzylformhydroxamic acid gave a characteristic copper salt.
3.  $\beta$ -Benzylformhydroxamic acid upon treatment with Beckmann's mixture suffered intramolecular oxidation in two directions giving carbon dioxide and benzyl amine in the one case, and formamide and benzaldehyde in the other.
4.  $\beta$ -Benzylformhydroxamic acid, upon treatment with phosphorus pentoxide, suffered intramolecular oxidation giving benzylisocyanate.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

### A NEW CLASS OF PHTHALEINS—MIXED PHTHALEINS— FORMED BY HEATING *p*-HYDROXYBENZOYL-*o*- BENZOIC ACID WITH PHENOLS.

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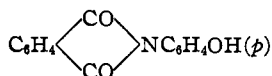
**Phenolphthaleinoxime and the Preparation of *p*-Hydroxybenzoyl-*o*-benzoic Acid.**—Phenolphthaleinoxime was prepared by Friedländer's<sup>1</sup> method. The following proportions of the materials employed were found to be advantageous: 50 g. phenolphthalein, 50 g. potassium hydroxide, 500 cc. water and 12.5 g. hydroxylamine hydrochloride (calculated 10.9 g.). It was found best to follow the course of the reaction with frequent tests made by withdrawing a small portion of the alkaline liquid from the flask while heating in the water bath to  $80^{\circ}$ , neutralizing with acetic acid and filtering off the precipitated oxime. When the filtrate, on addition of alkali, gives no color or only a faint pink the flask should be removed from the water bath, 100 cc. alcohol added, and the whole treated with acetic acid until slightly acid. The oxime is thus obtained pure as a sulfur-yellow precipitate, easily filtered. It should be washed with at least 500 cc. hot distilled water and allowed to dry in the air. The yield is quantitative.

The oxime prepared in this manner dissolves readily and *completely* in boiling dilute sulfuric acid (1 to 8), giving a bright yellow solution. When this solution has boiled from five to ten minutes, the color fades and white flakes appear on the surface. After this is observed, the boil-

<sup>1</sup> *Ber.*, 26, 172 (1893).

ing should be continued for about five minutes to insure the complete decomposition of the oxime. On cooling, the amount of the white crystalline substance increases. After filtering and recrystallizing once from hot water, small snow-white crystals of *p*-hydroxybenzoyl-*o*-benzoic acid are obtained, which melt with evolution of gas at 213°. The mother liquor from the crude acid, when neutralized with sodium carbonate, yields a finely divided, almost colorless, precipitate of *p*-aminophenol, that when crystallized from ether melts at 184°. The yield of both substances is quantitative, that is, 50 g. of phenolphthaleinoxime gave 35.8 g. of *p*-hydroxybenzoyl-*o*-benzoic acid and 14 g. of *p*-aminophenol (calculated 36.3 g. of *p*-hydroxybenzoyl-*o*-benzoic acid and 16.4 g. of *p*-aminophenol).

When a larger amount of hydroxylamine hydrochloride was used, 15 g. to 50 g. phenolphthalein, as recommended by Friedländer, the oxime was found to be contaminated with a substance which did not dissolve in dilute sulfuric acid. It was separated from the acid decomposition product of the oxime by extracting with hot water in which the *p*-hydroxybenzoyl-*o*-benzoic acid is soluble. After drying the insoluble residue, it was recrystallized from ethyl acetate, giving fine needles that melt at 288° with decomposition. Recrystallization from dilute alcohol yielded a product having the same melting point. It was identical in all respects with the *p*-hydroxyphthalanil



described by Piutti.<sup>1</sup> The same substance was obtained by Hans Meyer<sup>2</sup> by heating phenolphthaleinoxime with hydroxylamine hydrochloride. The following conditions seem to be favorable for its formation in the preparation of the oxime: (a) an excess of hydroxylamine, (b) prolonged heating of the alkaline reaction mixture (page 690).

Attempts were also made to prepare *p*-hydroxybenzoyl-*o*-benzoic acid from phthalic anhydride and phenol, both with and without boric acid and other condensing agents, but the results were negative.

**Diacetate of *p*-Hydroxybenzoyl-*o*-benzoic Acid.**—This substance was prepared by boiling one part of the pure acid with six parts of acetic anhydride. The excess of acetic anhydride was removed by boiling with ethyl alcohol, part of the liquid distilled off and the acetate precipitated with water. The dried product was recrystallized from 95% alcohol, which yielded a white crystalline substance, melting at 137–140°. A sharper melting point could not be obtained. Analyses of the crystals gave the following results:

<sup>1</sup> *Gazz. chim. ital.*, 16, 252 (1886).

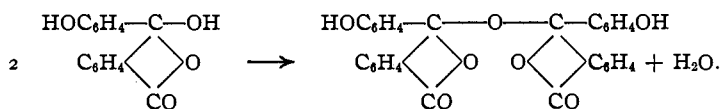
<sup>2</sup> *Monatsh.*, 20, 346 (1899).

Subst., (I) 0.2050, (II) 0.2561; H<sub>2</sub>O, (I) 0.0817, (II) 0.1037; CO<sub>2</sub>, (I) 0.4970, (II) 0.6205.

Calc. for C<sub>18</sub>H<sub>14</sub>O<sub>8</sub>: C, 66.24; H, 4.33. Found: (I) C, 66.14; H, 4.46; (II) C, 66.10; H, 4.53.

The diacetate is fairly soluble in ethyl alcohol but only slightly soluble in boiling methyl alcohol. It is very soluble in cold acetone, benzene and glacial acetic acid. It is insoluble in dilute aqueous alkali, but dissolves readily in alcoholic alkali, due to hydrolysis.

**Anhydride of *p*-Hydroxybenzoyl-*o*-benzoic Acid.**—This substance was prepared by heating 6 g. of *p*-hydroxybenzoyl-*o*-benzoic acid on a metal bath to a temperature of 200–204° for two hours. Water vapor was evolved and the substance became brown and viscous. The reaction mixture was dissolved in aqueous alkali. It gave a deep greenish blue solution which also had a red tinge. The color faded on standing. When acidified, white amorphous flocks were precipitated which, when filtered off and dried, melted at 170–180°. Six grams of *p*-hydroxybenzoyl-*o*-benzoic acid gave 5.3 g. of the anhydride (calculated 5.8 g.). This shows that two molecules of the acid have condensed with the elimination of one molecule of water.



The anhydride could not be purified by recrystallization. It was therefore boiled with acetic anhydride for three hours in the hope of obtaining an acetate, and the excess of the anhydride removed by boiling with alcohol. On cooling, almost colorless crystals separated which melted at 199–201°. These, when dried at 125° to constant weight, lost moisture, the weight of which corresponded to one molecule of water of crystallization. The dry substance was analyzed.

Subst., (I) 0.1314, (II) 0.1525; CO<sub>2</sub>, (I) 0.3475, (II) 0.4044; H<sub>2</sub>O, (I) 0.0511, (II) 0.0571.

Calc. for C<sub>28</sub>H<sub>18</sub>O<sub>7</sub>: C, 72.09; H, 3.89. Found: (I) C, 72.14; H, 4.35; (II) C, 72.34; H, 4.19.

The product is therefore the anhydride and not an acetate. It dissolves slowly in hot aqueous alkali, with a not very intense green color, but with no red tinge. Some of the last fractions of the product from the acetic anhydride and alcohol mixture dissolved in alcoholic alkali with the marked red color of an alkaline solution of phenolphthalein. This shows that the treatment with acetic anhydride freed the anhydride from a small quantity of phenolphthalein which was formed in the condensation. The pure anhydride of *p*-hydroxybenzoyl-*o*-benzoic acid is slightly soluble in hot absolute alcohol, but insoluble in methyl alcohol and ether. It is very soluble in acetone, chloroform and acetic acid. It is slightly

soluble in benzene, which converts it into an oil. It is soluble in concentrated sulfuric acid with an orange-red color. As it dissolves in alkalis with color and is precipitated by acids unchanged like the phthaleins it is represented as an ether-like anhydride similar to diglycolic acid. Graebe<sup>1</sup> states that he has made an anhydride of dihydroxybenzoylbenzoic acid to which he gives a similar formula (page 694).

**Phenolphthalein.**—*p*-Hydroxybenzoyl-*o*-benzoic acid was condensed with phenol by heating with an excess of the latter on a metal bath for several hours to 180°. The reaction product was distilled in steam to remove the excess of phenol, and the oily solid thus obtained dissolved in alkali. It gave the cherry-red solution with a slight bluish tinge, characteristic of phenolphthalein. On acidifying the filtered solution, a white amorphous precipitate was obtained. This was filtered off, washed and dried, and recrystallized from methyl alcohol. The yield is quantitative. White crusts were obtained that melted at 254–256°, the melting point of phenolphthalein. A diacetate<sup>2</sup> was obtained by boiling with acetic anhydride for two hours and then precipitating with water. The product when recrystallized from methyl alcohol melted at 141–143°, and showed all the other characteristic properties of phenolphthalein diacetate. A dibenzoate was prepared by the Bauman-Schotten method used by Bistrzycki and Nencki.<sup>3</sup> The product crystallized from benzene agreed with their description of phenolphthalein dibenzoate and melted at 168–169°, after driving off the benzene of crystallization. Hence *p*-hydroxybenzoyl-*o*-benzoic acid condenses with phenol, *without a condensing agent*, and gives a quantitative yield of phenolphthalein. *No isomeric compound is formed.* It is highly probable, therefore, that in phenolphthalein both hydroxyl groups occupy the para-positions to the phthalic acid residue. It also seems likely that *p*-hydroxybenzoyl-*o*-benzoic acid is the first product formed in the preparation of phenolphthalein (page 692) from phenol and phthalic anhydride.

**Phenolanilinephthalein Anilide.**—It was intended to prepare phenolanilinephthalein but the anilide of the phthalein was obtained. Three grams of *p*-hydroxybenzoyl-*o*-benzoic acid were heated with 2 g. of aniline on a metal bath for two and one-half hours at a temperature of 180°. About 1 g. zinc chloride was used as a condensing agent. The reaction product was viscous and of a dark brown color. It was distilled in steam to remove excess aniline and dissolve out the zinc chloride. A dark brown insoluble solid was thus obtained. This was dried and recrystallized from 95% alcohol. Fine colorless needles separated on cooling the hot alcoholic solution, which after several recrystallizations melted with de-

<sup>1</sup> *Arch. sci. phys. nat.*, 2, 91 (1893).

<sup>2</sup> *Ann.*, 202, 68 (1880).

<sup>3</sup> *Ber.*, 29, 132 (1896).

composition at 252–256°. The substance contained no solvent of crystallization and gave the following results on analysis by the Kjeldahl method:

Subst., (I) 0.2005; (II) 0.2501; cc. 0.1 *N* HCl, (I) 10.45; (II) 12.92.

Calc. for  $C_{26}H_{20}O_2N_2$ : N, 7.14. Found: N, (I) 7.30, (II) 7.24.

The anilide is insoluble in benzene and ether. It is soluble in cold acetone, methyl alcohol and ethyl alcohol. It dissolves on boiling with alkalis, giving a bluish red color similar to that of an alkaline solution of phenolphthalein but much less intense. This color is due to the hydrolysis of the anilide and the formation of the alkaline salt of the phenol-anilinephthalein (page 693). The phthalein is precipitated from this alkaline solution by acids in brown flocks.

**Phenolresorcinolphthaleins.**—Five grams *p*-hydroxybenzoyl-*o*-benzoic acid and 5 g. of resorcinol were heated together on a metal bath to a temperature of 160–170°. Water vapor was freely evolved and the reaction mixture became colored a yellowish brown. Heating was continued for three hours. The crude product was dissolved in alcohol and distilled in steam until no test for resorcinol was obtained in the distillate. On cooling, the crude condensation product was obtained as a bright orange-yellow oily solid which on drying became hard and brittle. It was extremely soluble in all organic solvents and to a considerable extent in water. It melted at 50–60°. This crude product was converted into a mixture of the triacetates by boiling three hours with one part sodium acetate and six parts acetic anhydride and this purified (page 684). The mixture of phthaleins obtained by hydrolyzing the pure triacetates with aqueous caustic soda and acidifying the clear deep red solution is an amorphous, almost gelatinous, pale yellow precipitate. This, when filtered off, washed thoroughly and dried, was recrystallized from acetone. The crystals from the acetone solution can easily be separated into two crops. The first crop consists of fine white needles that melt at 200–202°. The second crop consists of a somewhat smaller amount of thicker needles or plates which can be obtained pure white by three recrystallizations from acetone. They melt at 270–272°, with decomposition. The substance melting at 200–202° was heated at 125° for three hours. It lost some weight but less than the calculated amount for one molecule of acetone of crystallization. The melting point did not change. These crystals were analyzed after heating to constant weight at 125°.

Subst., (I) 0.1493, (II) 0.1561;  $CO_2$ , (I) 0.3926, (II) 0.4117;  $H_2O$ , (I) 0.0618, (II) 0.0600.

Calc. for  $C_{26}H_{14}O_5$ : C, 71.84; H, 4.22. Found: (I) C, 71.74; H, 4.63; (II) C, 71.92; H, 4.30.

The analyses and method of formation show it to be a phenolresorcinolphthalein. It is very soluble in all organic solvents except acetone, in

which it is easily soluble when amorphous but only slightly soluble when crystalline. It dissolves in alkalis with a deep wine-red color, which fades rapidly in the presence of an excess of alkali, but does not fade perceptibly on standing several days with dilute alkali. It dissolves in concentrated sulfuric acid with a deep red color, similar to the color of the alkaline solution. It represents 60 to 65% of the product obtained by hydrolyzing the mixture of the pure triacetates.

The substance melting at  $270-272^{\circ}$  is much more difficult to purify than the first product, on account of its far greater solubility in acetone and other solvents. A pure white, well-crystallized product was finally obtained by three recrystallizations from acetone. It was heated to  $125^{\circ}$  for three hours and lost only a small amount of weight. This product was analyzed:

Subst., 0.1352;  $\text{CO}_2$ , 0.3572;  $\text{H}_2\text{O}$ , 0.0532.

Calc. for  $\text{C}_{20}\text{H}_{14}\text{O}_6$ : C, 71.84; H, 4.22. Found: C, 72.07; H, 4.40.

According to this analysis and the method of formation the substance is a second phenolresorcinolphthalein. It is obtained in smaller amount than its isomer. Analyses made on a less pure product gave figures for carbon considerably too high for the calculated value, assuming the substance to be phenolresorcinolphthalein. It is obtained as part of the product of hydrolysis of the pure triacetates of the phenolresorcinolphthaleins described further on. It dissolves in alkalis and in concentrated sulfuric acid with the same color as the lower melting isomer. Both phthaleins are precipitated by acids from the alkaline solution in almost colorless flocks.

**Triacetates of the Phenolresorcinolphthaleins.**—When the crude product of condensation between resorcinol and *p*-hydroxybenzoyl-*o*-benzoic acid was boiled several hours with acetic anhydride, a substance was obtained which, after crystallization from absolute alcohol, gave the following results on analysis:

Subst., (I) 0.1725, (II) 0.1948;  $\text{CO}_2$ , (I) 0.4409, (II) 0.4979;  $\text{H}_2\text{O}$ , (I) 0.0698, (II) 0.0730.

Calc. for  $\text{C}_{20}\text{H}_{13}\text{O}_6(\text{COCH}_3)$ : C, 70.20; H, 4.29; for  $\text{C}_{20}\text{H}_{12}\text{O}_6(\text{COCH}_3)_2$ : C, 68.88; H, 4.34; for  $\text{C}_{20}\text{H}_{11}\text{O}_6(\text{COCH}_3)_3$ : C, 67.81; H, 4.38. Found: C, (I) 69.73; H, 4.53; C, (II) 69.73; H, 4.19.

Apparently a mixture of the monoacetates and the diacetates is present. This product was pure white and melted at  $160-164^{\circ}$ . It was boiled for three hours with one part sodium acetate and five parts acetic anhydride. The solution was poured into water and allowed to stand overnight. The solid substance was filtered off, washed and dried. It was recrystallized from absolute alcohol, giving fine snow-white needles melting at  $162-165^{\circ}$ . These were recrystallized from acetone, which yielded finer white needles melting at  $175-180^{\circ}$ . No sharp melting point could be ob-

tained and a change of melting point occurred with each change of solvent. The product was heated at  $120^{\circ}$  to constant weight and analyzed:

Subst., (I) 0.1817, (II) 0.1736;  $\text{CO}_2$ , (I) 0.4510, (II) 0.4326;  $\text{H}_2\text{O}$ , (I) 0.0668, (II) 0.0703.

Calc. for  $\text{C}_{20}\text{H}_{11}\text{O}_6(\text{OCCH}_3)_3$ : C, 67.81; H, 4.38. Found: C, (I) 67.71; H, 4.11; C, (II) 67.98; H, 4.53.

These figures agree closely with the calculated values for the triacetate of phenolresorcinolphthalein, and, taking into consideration the changing melting points, the substance is a mixture of the triacetates of the two phenolresorcinolphthaleins. It is soluble in most organic solvents, but not very soluble in methyl and ethyl alcohols when pure. It is fairly soluble in acetone. It is slowly hydrolyzed on boiling with aqueous alkali but readily if alcoholic alkali is used. It dissolves in concentrated sulfuric acid, with a deep red color, probably first undergoing hydrolysis.

**$\alpha$ -Naphtholphthalein.**—This substance was prepared by heating 5 g. of *p*-hydroxybenzoyl-*o*-benzoic acid with 4 g. of  $\alpha$ -naphthol (calculated 3.0 g.) for three hours at  $130$ – $150^{\circ}$ . The reaction product had a dark brown color. It was distilled in steam to remove the excess of  $\alpha$ -naphthol. A light brown oily substance was thus obtained which solidified on cooling. It dissolves fairly readily in alkali, giving a deep blue color. Acids precipitated it from this solution in light brownish flocks. These, when dried in the air, melted at  $100$ – $120^{\circ}$ . The crude substance is easily soluble in cold methyl and ethyl alcohols, ether and glacial acetic acid. It is slightly soluble in benzene, which converts it into an oil. It dissolves in concentrated sulfuric acid with a deep green color. It gives a diacetate on boiling with acetic anhydride. The pure acetate was hydrolyzed by passing steam into the substance suspended in dilute alcoholic alkali. When the deep blue solution was acidified, brown flocks were precipitated. These, when dry, melted at  $110$ – $130^{\circ}$ . The solubilities were the same as described above for the crude phthalein. All attempts to crystallize the substance failed and a comparatively pure amorphous product could not be obtained.

**$\alpha$ -Naphtholphthalein Diacetate.**—This substance was obtained by boiling the crude phthalein with an excess of acetic anhydride for two hours. The excess of acetic anhydride was removed by boiling with alcohol and the solution poured into a large quantity of cold water. A brownish amorphous precipitate was obtained. This was recrystallized from absolute ethyl alcohol many times. An attempt was made to remove the brownish color by boiling with animal charcoal but this was unsuccessful. The product finally obtained had a light yellowish brown color. It was fairly soluble in absolute alcohol and melted at  $188$ – $190^{\circ}$ . A sharper melting point could not be obtained. The diacetate contains no solvent of crystallization. When dried at  $120^{\circ}$  it loses a small amount

of moisture that appears to be mechanically held. Samples dried at  $120^{\circ}$  were analyzed.

Subst., (I) 0.1765, (II) 0.1614;  $\text{CO}_2$ , (I) 0.4800, (II) 0.4385;  $\text{H}_2\text{O}$ , (I) 0.0667, (II) 0.0610.

Calc. for  $\text{C}_{28}\text{H}_{20}\text{O}_6$ : C, 74.32; H, 4.46. Found: C, (I) 74.19; H, 4.23; C, (II) 74.12; H, 4.23.

The diacetate is soluble in cold benzene and acetone and fairly soluble in hot methyl and ethyl alcohols. It crystallizes from absolute alcohol in fine feathery crystals. It is insoluble in cold aqueous alkali, but soluble with a blue color on boiling. It dissolves in concentrated sulfuric acid with a deep green color due to hydrolysis.

**$\beta$ -Naphtholpheno-phthalein.**—Five grams of *p*-hydroxybenzoyl-*o*-benzoic acid were heated on a metal bath with 4 g.  $\beta$ -naphthol (calculated 3.0 g.) at a temperature of  $150$ – $160^{\circ}$  for three hours. Water vapor was freely evolved and a brown viscous reaction product was obtained. This was dissolved in normal aqueous alkali, giving a deep green color. When the filtered alkaline solution was acidified, brown flocks were precipitated. It was found impossible to purify this product or its acetate, obtained by boiling the crude phthalein with acetic anhydride.

**Condensation of *p*-Hydroxybenzoyl-*o*-benzoic Acid with the Cresols.**—*p*-Hydroxybenzoyl-*o*-benzoic acid was condensed with *o*-cresol, with *m*-cresol and with *p*-cresol by the same method described in the cases of the other phthaleins. Products were obtained which gave, respectively, violet-red, violet and blue solutions with alkalis. An attempt has been made to purify these products, but the work is not complete at the present time.

***p*-Methoxybenzoyl-*o*-tetrachlorobenzoic Acid.**—This acid was prepared by condensing tetrachlorophthalic anhydride with anisol in the presence of aluminum chloride. Ten grams of the anhydride were added to 25 cc. anisol and 25 g. powdered aluminum chloride were slowly added to the mixture. A vigorous reaction took place in the cold, the contents of the flask becoming dark red or purple. Twenty-five grams more of the aluminum chloride were then added and the whole warmed on the water bath for one hour. The contents of the flask were then poured into water which precipitated a white amorphous solid. Distillation in steam removed the excess of anisol, without dissolving the solid product. This was filtered off while still warm, and extracted with caustic soda solution, in which a small portion of the solid was insoluble. On cooling the hot alkaline solution, a white crystalline sodium salt separated which was removed by filtering. This was purified by recrystallization from hot water and the solution of the pure salt decomposed with hydrochloric acid. An insoluble white solid was immediately thrown out of solution. It was dried and recrystallized from ben-



zene, in which it is fairly soluble. Fine, white needles were thus obtained containing one-half molecule benzene of crystallization and melting at  $182^{\circ}$ . If, however, the capillary tube containing the substance is quickly heated, the acid melts at  $125^{\circ}$ , gas being evolved. A slow gradual heating shows a melting point at  $182^{\circ}$ , as stated above. Analysis of the product heated to constant weight at  $120^{\circ}$  gave the following results:

Subst., (I) 0.1570, (II) 0.1642; cc. 0.1 *N* AgNO<sub>3</sub>, (I) 15.97, (II) 16.64.

Calc. for C<sub>15</sub>H<sub>9</sub>O<sub>4</sub>Cl<sub>4</sub>: Cl, 36.00. Found: Cl, (I) 36.07; (II) 35.94.

The acid is very soluble in most organic solvents but only fairly soluble in hot benzene, insoluble in cold benzene. It is completely insoluble in water and ligroin. The pure amorphous acid obtained by decomposing the pure aqueous solution of its sodium salt with acid melts vaguely from  $170$ – $175^{\circ}$ . One crystallization of this product from benzene brings the melting point to  $182^{\circ}$ . The substance after heating to  $120^{\circ}$  for two hours also melts at  $182^{\circ}$ .

The insoluble residue left after extracting the crude solid reaction product with alkali was washed, dried and recrystallized from alcohol. When the hot alcoholic solution was cooled, colorless needles separated, melting at  $152^{\circ}$ . These were identical in all other respects with the dimethyl ether of phenoltetrachlorophthalein prepared by Orndorff and Black<sup>1</sup> by another method.

**Sodium Salt of *p*-Methoxybenzoyl-*o*-tetrachlorobenzoic Acid.**—This salt is obtained as described above in the preparation of the free acid. It crystallizes from water in shining, mother-of-pearl leaflets that melt with decomposition at  $275^{\circ}$ . The salt crystallizes with five molecules of water of crystallization and loses its crystalline form when dried.

Subst., (I) 0.1398, (II) 0.1343; loss after 3 hrs. at  $130^{\circ}$ , (I) 0.0243; loss after 2 hrs. at  $140^{\circ}$ , (II) 0.0238.

Calc. for C<sub>15</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>Na.5H<sub>2</sub>O: H<sub>2</sub>O, 17.80. Found: H<sub>2</sub>O, (I) 17.38, (II) 17.72.

Part of the water of crystallization is easily lost on standing at room temperature. A specimen allowed to stand overnight gave figures corresponding to three and one-half molecules water.

Subst., (I) 0.1473, (II) 0.1608; loss after 3 hrs. at  $130^{\circ}$ , (I) 0.0195; loss after 2 hrs. at  $130^{\circ}$ , (II) 0.0212.

Calc. for C<sub>15</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>Na.3 $\frac{1}{2}$ H<sub>2</sub>O: H<sub>2</sub>O, 13.16. Found: H<sub>2</sub>O, (I) 13.24, (II) 13.18.

The anhydrous material was analyzed for sodium by fuming down with concentrated sulphuric acid.

Subst., (I) 0.1278, (II) 0.1396; Na<sub>2</sub>SO<sub>4</sub>, (I) 0.0221, (II) 0.0245.

Calc. for C<sub>15</sub>H<sub>7</sub>O<sub>4</sub>Cl<sub>4</sub>Na: Na, 5.53. Found: Na, (I) 5.60, (II) 5.68.

**Potassium Salt of *p*-Methoxybenzoyl-*o*-tetrachlorobenzoic Acid.**—The potassium salt was prepared by dissolving the pure acid in dilute

<sup>1</sup> *Am. Chem. J.*, 41, 374 (1909).

aqueous caustic potash at the boiling point of the solution. On cooling the filtered solution the potassium salt separated. It crystallizes from water in small, shining leaflets, without the marked luster of the sodium salt. These melt at 245–248° with decomposition, if the water of crystallization has been removed. If not, the melting point is 145° without decomposition. That is, the substance melts in its own water of crystallization. It contains four molecules of water of crystallization.

Subst., (I) 0.1401, (II) 0.1612; loss after 3 hrs. at 125°, (I) 0.0192, (II) 0.0225.  
Calc. for  $C_{15}H_7O_4Cl_4K \cdot 4H_2O$ :  $H_2O$ ; 14.29. Found:  $H_2O$ , (I) 13.70, (II) 13.96.

Part of the water of crystallization is lost on standing, as in the case of the sodium salt. The anhydrous material was analyzed for potassium by fuming down with concentrated sulphuric acid.

Subst., (I) 0.1380, (II) 0.1475;  $K_2SO_4$ , (I) 0.0271, (II) 0.0291.  
Calc. for  $C_{15}H_7Cl_4K$ : K, 9.05. Found: K, (I) 8.81, (II) 8.85.

**Acetate of *p*-Methoxybenzoyl-*o*-tetrachlorobenzoic Acid.**—One part *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid was boiled one-half hour with three parts acetic anhydride. Alcohol was added and the solution allowed to cool. Fine, white needles separated which melted sharply at 225°. The substance was recrystallized from a mixture of glacial acetic acid and ethyl alcohol. The melting point did not change. The acetate loses no weight when dried at 150°, differing greatly in this respect from the acetate of benzoyl-*o*-tetrachlorobenzoic acid which loses weight when heated to 100°. The air-dried substance was analyzed for chlorine.

Subst., (I) 0.1740, (II) 0.1356; cc. 0.1 *N*  $AgNO_3$ , (I) 15.99, (II) 12.43.  
Calc. for  $C_{17}H_{10}O_8Cl_4$ : Cl, 32.53. Found: Cl, (I) 32.59, (II) 32.51.

The acetate is slightly soluble in hot methyl and ethyl alcohols, soluble in hot glacial acetic acid and soluble in cold benzene and acetone. It is insoluble in boiling aqueous alkalies but easily soluble in alcoholic alkali. When heated with phenol it forms the monomethyl ether of phenoltetrachlorophthalein.

**Monomethyl Ether of Phenoltetrachlorophthalein.**—One part of the acetate of *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid was heated on a metal bath with two parts of phenol at the boiling point of the mixture, about 180°, for seven hours. The brown viscous reaction mixture was distilled in steam to remove the excess of phenol and the insoluble residue thus obtained was extracted with normal caustic soda. A small part of the material was found to be insoluble in the hot aqueous alkali. This was recrystallized from glacial acetic acid giving white crystals of the acetate melting at 222–225°. The reaction between the acetate and the phenol was not complete, some of the acetate remaining unchanged. The alkaline extract was of a not very intense brownish red color. It was acidified, giving a white, amorphous precipitate. This was dried

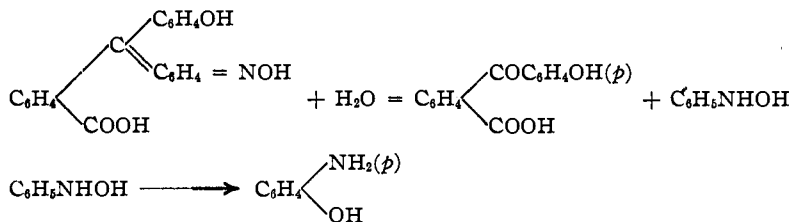
and recrystallized from 95% ethyl alcohol. Fine, white needle clusters separated, which after several recrystallizations melted at 295°, with decomposition, the substance darkening in color above 260°. It contained no solvent of crystallization. Analyses gave the following results:

Subst., (I) 0.1541, (II) 0.2203; cc. 0.1 *N* AgNO<sub>3</sub>, (I) 13.06, (II) 18.71  
Calc. for C<sub>21</sub>H<sub>12</sub>O<sub>5</sub>Cl<sub>4</sub>: Cl, 30.18. Found: Cl, (I) 30.05, (II) 30.12

The monomethyl ether of phenoltetrachlorophthalein is insoluble in cold normal caustic soda solution, but dissolves on boiling with a brownish red color, which on cooling becomes violet-red. The color is not very intense. The pure compound is fairly soluble in hot ethyl alcohol, more so in methyl alcohol. It is very soluble in benzene and acetone. It dissolves slowly in hot sulphuric acid with a deep pink color.

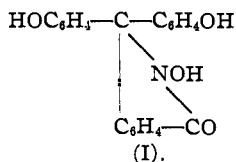
### Theoretical.

In order to explain the quantitative decomposition of phenolphthalein-oxime into *p*-hydroxybenzoyl-*o*-benzoic acid and *p*-aminophenol, an internal rearrangement of the phenolphthalein-oxime molecule must be assumed before hydrolysis takes place. Friedländer<sup>1</sup> represented the decomposition by the following equation:



The phenylhydroxylamine first formed is assumed to undergo rearrangement giving *p*-aminophenol.

If we assume that the oxime has the following structure, for which there is good evidence,



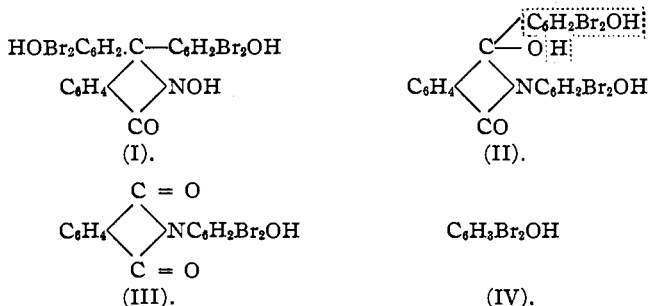
Phenolphthalein-oxime.

and that it undergoes the Beckmann rearrangement analogous to that of the ketone oximes, we will have, first, a shifting of the OH group from the nitrogen to the methane carbon atom and one of the phenol residues, C<sub>6</sub>H<sub>4</sub>OH, taking its place as shown in Formula II.

<sup>1</sup> *Ber.*, 26, 172 (1893). This formula was later abandoned by Friedländer himself. See *Ibid.*, 28, 3258 (1895).

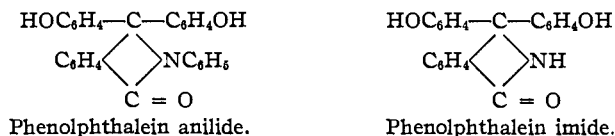


dibromo-derivative could be made from the oxime and hydroxylamine in alkaline solution. The explanation of this reaction is very simple, if we assume Formula I for the oxime.



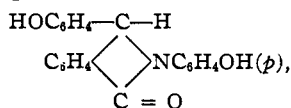
The Beckmann rearrangement gives (II), which by the loss of dibromophenol (IV) gives the dibromo-derivative of *p*-hydroxyphthalanil (III).

This formula for the oxime (page 689) is analogous to that of the anilide and of the imide.

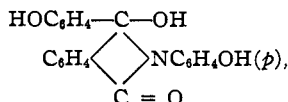


Compounds formed in a similar manner from phenolphthalein, one from aniline and the other from ammonia. That these compounds do not hydrolyze or reduce as readily as the oxime is easily explained on the ground that they do not undergo the Beckmann rearrangement.

The formation of the reduction product of phenolphthaleinoxime, which Hans Meyer has proved to have the structure



may also be regarded as a confirmation of the formula here given for the oxime. Before the reduction takes place the Beckmann rearrangement of the oxime gives



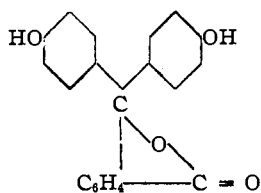
which would reduce at once to the above compound. There are no facts known regarding the oxime which can not be explained better by this formula than by any other<sup>1</sup> which has been proposed.

<sup>1</sup> See R. Meyer and Kissin, *Ber.*, 42, 2825 (1909); also Orndorff and Pratt, *Am. Chem. J.*, 47, 89 (1912).

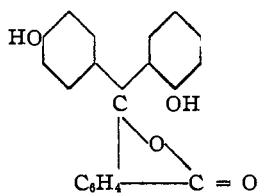
Since the hydroxyl groups in both *p*-hydroxybenzoyl-*o*-benzoic acid and in *p*-aminophenol are *undoubtedly* in the *p*-positions, it follows that they must occupy the *p*-positions in phenolphthalein also. Phenolphthalein is therefore *not* a mixture of two isomers as might be inferred from the fact that fluoran, the anhydride of diorthophenolphthalein, is always formed in the preparation of phenolphthalein from phenol and phthalic anhydride in the presence of sulfuric acid. That is, since in this condensation a diortho- as well as a dipara-compound is formed, there is certainly a possibility that a para-ortho compound might also be formed. This conclusion regarding the structure of phenolphthalein is also in accord with that found by J. J. Kennedy<sup>1</sup> in the case of phenoltetrachlorophthalein.

The easy and quantitative conversion of *p*-hydroxybenzoyl-*o*-benzoic acid into phenolphthalein by heating the acid alone with phenol, is a proof of the extreme reactivity of this acid towards phenol. The result of this condensation supports the theory that *p*-hydroxybenzoyl-*o*-benzoic acid is indeed an intermediate product in the formation of phenolphthalein from phthalic acid anhydride and phenol. In the preparation of phenolphthalein a large excess of phenol is used. This would combine at once with the *p*-hydroxybenzoyl-*o*-benzoic acid to form phenolphthalein and so it is not surprising that this acid has not been obtained in the preparation of phenolphthalein.

It is evident that the condensation of *p*-hydroxybenzoyl-*o*-benzoic acid with phenol must result in the formation of phenolphthalein or an isomer, according as the acid residue enters para or ortho to the phenol hydroxyl group.



Diparaphenolphthalein.

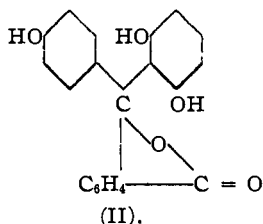
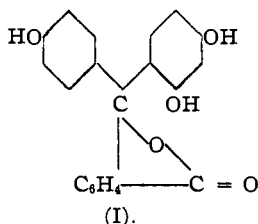


Paraorthophenolphthalein.

The fact that no isomer is formed and that the product is identical with phenolphthalein indicates that this compound is a dipara-product. The paraortho-product has not yet been made.

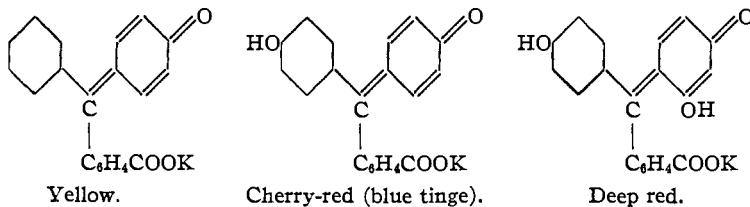
The acid is highly reactive towards other phenols also. Condensation with resorcinol results in the formation of two products, both of which by analyses are shown to be phenolresorcinolphthaleins. The existence of isomers of such a constitution can only be explained by the following formulas:

<sup>1</sup> THIS JOURNAL, 38, 248 (1916).

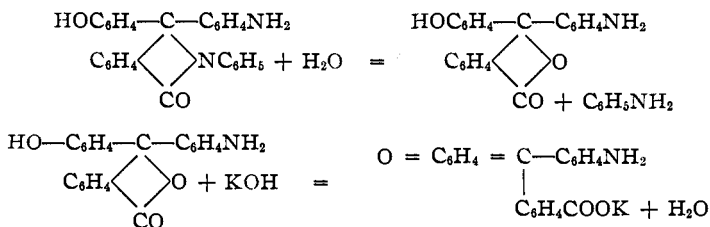


The fact that these substances were obtained by hydrolyzing a mixture of the *pure* triacetates (which, however, did not possess a definite melting point) is a point in favor of the correctness of the formulas. The product obtained by boiling the crude phthaleins with acetic anhydride alone appears to be a mixture of mono- and diacetates. It is possible that the hydroxyl-groups para to the methane carbon atom are more readily acetylated than those in the ortho positions. Formula I probably represents the lower melting phthalein obtained in larger amount.

The extremely deep red color of the alkaline solution is probably due to the presence of the three hydroxyl groups in the molecule. The effect of the introduction of one, two and three hydroxyl groups into the benzene residues of diphenylphthalide may be shown by a comparison of the colors of the alkaline solutions of monohydroxydiphenylphthalide, phenolphthalein and phenolresorcinolphthalein.

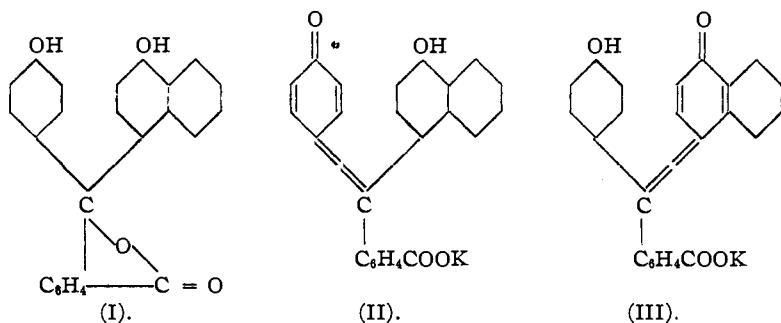


The red color obtained by boiling phenolanilinephthaleinanilide with aqueous alkali must be due to the hydrolysis of the anilide giving a salt of phenolanilinephthalein and aniline,



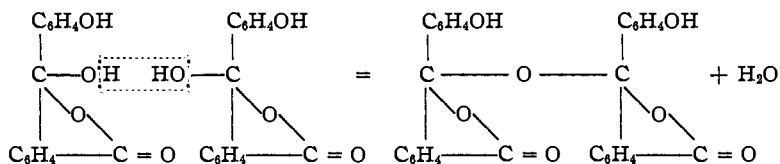
since the anilide of phenolphthalein is soluble in alkalis without color. The presence of an amino and a hydroxyl group have an effect on the color of the salt similar to that of two hydroxyl groups.

$\alpha$ -Naphtholphthalalein may be represented by Formula I and its colored salt by Formulas II or III.

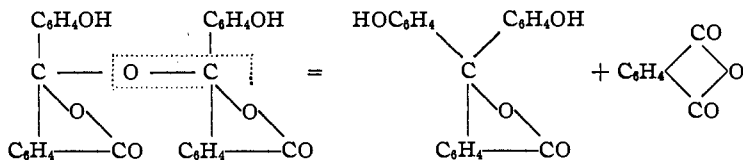


The fact that both the phthalalein and acetate are slightly colored is probably due to the presence of a small amount of an impurity.

When *p*-hydroxybenzoyl-*o*-benzoic acid is heated to 205°, water is evolved and the loss in weight corresponds practically quantitatively to the calculated loss of one molecule of water from two molecules of the acid. The formation of the anhydride may be represented as follows:



The resulting compound dissolves in alkalis with a green color that quickly fades on standing. The alkaline solution of the *crude* product had a marked reddish tinge, due to the presence of some phenolphthalein. The compound may be regarded as an ether-like anhydride of *p*-hydroxybenzoyl-*o*-benzoic acid. It breaks up on heating into phenolphthalein and phthalic anhydride,



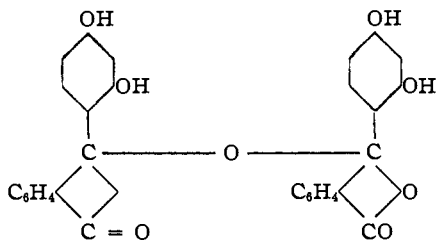
analogous to the decomposition of dihydroxybenzoyl-*o*-benzoic acid,<sup>1</sup> into fluorescein and phthalic anhydride.

Graebe<sup>2</sup> states that by the action of acetyl chloride on dihydroxybenzoyl-*o*-benzoic acid and saponification of the product formed he obtained a similar compound, to which he gives the formula

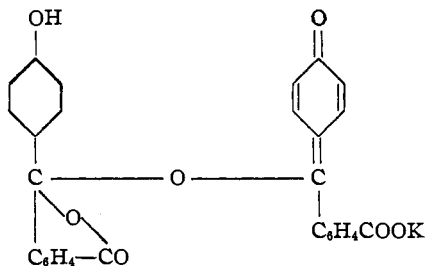
<sup>1</sup> Baeyer, *Ann.*, **183**, 23 (1876).

<sup>2</sup> *Arch. sci. phys. nat.*, **2**, 91 (1893).



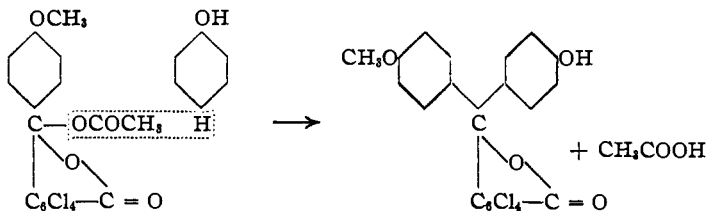


The colored salt of the anhydride probably has a quinoid constitution.



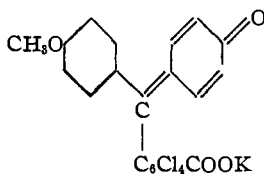
Since the anhydride is precipitated unchanged by addition of an acid to the alkaline solution, the union by means of the oxygen atom is a stable one. This renders it improbable that the product is an ordinary anhydride of *p*-hydroxybenzoyl-*o*-benzoic acid for such a substance would dissolve in alkalis without color and would give *p*-hydroxybenzoyl-*o*-benzoic acid when the alkaline solution was acidified.

The preparation of the monomethyl ether of phenoltetrachlorophthalein from the acetate of *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid by heating with phenol without a condensing agent is strictly analogous to the formation of *p*-hydroxydiphenyltetrachlorophthalide from *o*-benzoyltetrachlorobenzoic acid acetate and phenol.<sup>1</sup> The introduction of a methoxyl group into the molecule renders the acetate more stable, *i. e.*, the acetate of *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid is stable at 150° and the melting point observed, *i. e.*, 225°, is the true melting point of the acetate. On the contrary, the acetate of *o*-benzoyltetrachlorobenzoic acid is unstable at 96° and the melting point observed, 200°, is that of the acid, or its anhydride. The monomethyl ether of phenoltetrachlorophthalein is formed by the following reaction:



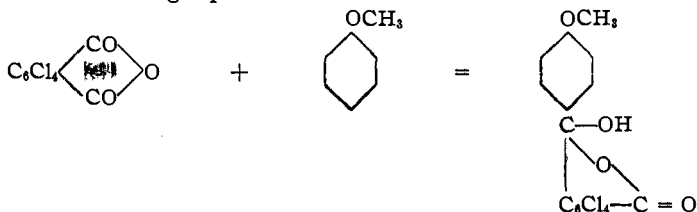
<sup>1</sup> THIS JOURNAL, 39, 293 (1917).

The colored salts of the ether may be explained by the usual quinoid formula

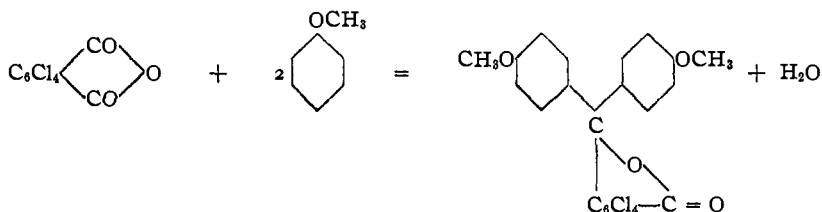


The methylation of one hydroxyl group reduces somewhat the intensity of the color of the alkaline salts as compared with those of the unmethylated phthalein.

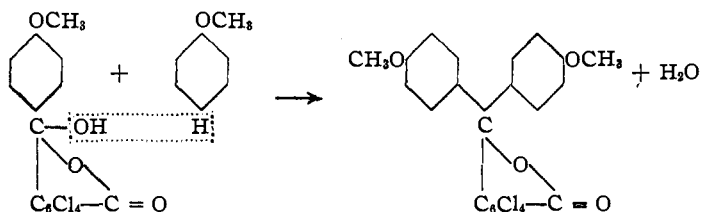
The condensation of anisol with tetrachlorophthalic anhydride in the presence of aluminum chloride to give *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid, a derivative of *o*-benzoylbenzoic acid, is easily understood from the following equation:



When two molecules of anisol react with one of tetrachlorophthalic anhydride, the dimethyl ether of phenoltetrachlorophthalein is formed.



Here as in the case of the formation of phenolphthalein it is probable that the reaction proceeds in two stages. First the *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid is formed as shown above and this then reacts with the second molecule of the anisol as shown below:



This product is identical with the dimethyl ether of phenoltetrachlorophthalein obtained by Orndorff and Black<sup>1</sup> by a different method.

### Summary.

1. A formula for phenolphthaleinoxime has been given which explains its quantitative decomposition into *p*-hydroxybenzoyl-*o*-benzoic acid and *p*-aminophenol and which is in better accord with all of the facts known in regard to the oxime than any other which has been proposed.

2. The preparation of phenolphthalein and of several mixed phthaleins from *p*-hydroxybenzoyl-*o*-benzoic acid has been accomplished.

3. Strong evidence has been obtained to show that the condensation of phenol and phthalic anhydride to give phenolphthalein takes place in two stages and that *p*-hydroxybenzoyl-*o*-benzoic acid is an intermediate product in this condensation.

4. The mixed phthaleins, like phenolphthalein itself, are purified with difficulty. It was found best to make and purify the acetates and by hydrolyzing the latter obtain the pure phthaleins.

5. The acetates of the phenolresorcinolphthaleins and of  $\alpha$ -naphtholphenolphthalein have been obtained pure.

6. The anilide of phenolanilinephthalein is formed instead of the phthalein when *p*-hydroxybenzoyl-*o*-benzoic acid is heated with aniline.

7. The two phenolresorcinolphthaleins have been obtained pure by hydrolyzing a mixture of the pure triacetates.

8. The product of the condensation of two molecules of *p*-hydroxybenzoyl-*o*-benzoic acid with the loss of a molecule of water has been studied. This ether-like anhydride resembles the phthaleins very closely and decomposes into phenolphthalein and phthalic acid anhydride when heated.

9. *p*-Methoxybenzoyl-*o*-tetrachlorobenzoic acid, and its sodium, and its potassium salts have been prepared and studied.

10. The acetate of *p*-methoxybenzoyl-*o*-tetrachlorobenzoic acid condenses with phenols to give the monomethyl ethers of the phthaleins. It probably possesses a lactone structure.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE.]

## THE ACTION OF THE TOLYL MUSTARD OILS ON SODIUM-PHENYLACETYLENE.

By DAVID E. WORRALL.

Received January 29, 1917.

It has long been known that the thioanilids react readily with hydroxylamine<sup>2</sup> through the elimination of hydrogen sulfide to form oximes.

<sup>1</sup> *Am. Chem. J.*, 41, 374 (1909).

<sup>2</sup> Müller, *Ber.*, 19, 1669 (1886).