a higher percentage of esterification and gives a distillate of the highest rotatory power.

3. The long refluxing at ordinary pressure and relatively high temperature gives the smallest percentage of distillate, the highest percentage of non-distillable residue, the highest percentage of esterification, uses up a large amount of ammonium chloride, and gives of course the highest degree of methylation, which means the highest percentage of dimethyl and other higher methylated derivatives, most of which will not crystallize.

4. The theory advanced by Werner to explain this reaction is the first and only correct one, all the observed facts, many of which he did not have, being in accord with his theory.

5. The 4 types of reaction agree with the principles of a larger theory, which applies to all organic reactions of this type in which a gas is evolved. This theory we are working out in a score of other cases.

6. Monomethylamine, a valuable reagent and the member of the series most often desired, is best made by the vacuum reflux method.

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PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR, XIV.[1] SOME DERIVATIVES OF TETRABROMOPHTHALIMIDE.

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Tetrabromophthalic anhydride has been prepared by the method previously described for the tetraiodo derivative.[2] From the resulting product a fairly comprehensive series of compounds related to the corresponding phthalimid has been made, by condensing the anhydride with various primary amines. These will be utilized at some future time in a study of their absorption spectra.

The tetrabromophthalimides follow closely in their general properties the tertachloro- and tetraiodo-analogues, with the differences that might be expected from the substitution of bromine for chlorine or iodine. The bromine derivatives show, to the eye, slightly more of a tendency toward yellow than the tetrachloro compounds, but less so than those containing iodine in the molecule. Similarly in the property of forming unstable, molecular addition products with various solvents and with tertiary amines, the brominated derivatives occupy a position intermediate between the compounds containing chlorine and those containing iodine. Whereas, tetraiodophthalic anhydride and its anils generally gave merely a slight color with dimethyl aniline, tetrabromophthalic anhydride separa-

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[1] THIS JOURNAL, 40, 198 (1918).

[2] *Ibid.*, 40, 254 (1018).

ted out of this solution in well-formed, high-colored crystals, which resemble those formed by tetrachlorophthalic anhydride. In a number of other cases anils were observed to crystallize from solution in the form of highly colored addition products with the solvent. It may be noted that these additions of solvents were not usually in simple ratio but generally from 1 : 3 up to 1 : 5.

No definite example of dimorphism was found among the tetrabromophthalanils, but from the fact that in many cases isomers crystallized in distinctly different forms, it is concluded that dimorphism existed, but that it was not possible to isolate the unstable modification. For instance, the *o*- and *m*-tolils crystallized as small colorless plates while the isomeric *p*-tolil gave long, hair-like, bright yellow needles. Also the *o*-ethoxy anil was obtained as small iridescent plates and the *p*-ethoxy anil in long filamentous crystals. The α-naphthylimide crystallized in the needle form, but the β- separated as plates.

Tetrabromophthalic Anhydride.—Bromination was carried out by dissolving 300 g. of phthalic anhydride in 5 lbs. of fuming sulfuric acid containing 50% free sulfur trioxide, adding 6 g. of iodine as a carrier and 460 cc. of bromine. The bromine was added in portions of 240, 120, 50 and 50 cc. After the first addition the mixture was heated in an oil bath to 70° until the bromine was absorbed, then cooled to room temperature and more bromine was added, after which the temperature was raised to 100°. This procedure was repeated, raising the temperature to 130° and finally to 170°, where it was maintained for about half an hour. After cooling, the mixture was poured over cracked ice. Impure tetrabromophthalic anhydride so obtained was purified by dissolving it in warm, dil. sodium hydroxide solution, filtering and reprecipitating by mineral acid. This gave tetrabromophthalic acid contaminated with considerable quantities of its mono sodium salt. To decompose this salt it was found necessary to steam the acidified solution vigorously for about half an hour before filtering off the tetrabromophthalic acid. The dried acid was then converted into its anhydride by crystallizing from xylene, in which it is soluble in the ratio of 1 : 6. 750–850 g. of anhydride melting at 273.5–274° (corr.), or about a 75–85% yield may be obtained. Lower brominated derivatives are effectually removed by the above procedure.

A small sample of tetrabromophthalic anhydride carefully purified by repeated crystallization from glacial acetic acid and xylene melted at 279.5–280.5° (corr.). It is quite soluble in nitro benzene (1 : 5), sparingly so in glacial acetic acid (1 : 50) and benzene.

Subst. 0.1791, 0.1906. Cc. 0.1 *N* $AgNO_3$; 15.48, 16.44.
Calc. for $C_8O_3Br_4$: Br, 68.92. Found: 69.08, 68.94.

Addition Product with Dimethylaniline.—Tetrabromophthalic anhydride is quite soluble in dimethylaniline giving an intensely red solution from which deep red, long blade-like crystals separate. This is an unstable addition product of the anhydride and dimethylaniline and loses the latter easily on standing in the air or upon washing with solvents. Unlike the 1 : 1 relation in the case of tetrachlor anhydride, the addition here seems to be that of two molecules of dimethylaniline with one of tetrabromonaphthalic anhydride. It was very difficult to obtain the crystals free from mother liquor and still prevent efflorescence. Exact analysis was also prevented because of the fact that last traces of dimethylaniline could not be removed even by prolonged heating at 130°. Sample I was prepared by drying fresh crystals with paper without crushing, exposing to the air for about 18 hours, and then obtaining the loss in weight after heating for 24 hours at 110°. Sample II was dried in a desiccator over fresh anhydride for 8 days and finally heated to 110° as before.

Subst. 1.1958, 1.4892. Loss (24 hours at 110°); 0.3574, 0.4586.

Calc. for $C_8O_3Br_4.C_6H_5N(CH_3)_2$: Loss, 34.50%. Calc. for $C_8O_3Br_4.C_6H_4N(CH_3)_2$: Loss, 20.85%. Found: 29.88, 30.80.

Tetrabromophthalimide.—Twenty g. of tetrabromophthalic anhydride was dissolved in 100 cc. of nitrobenzene and 20 g. of formamide added. The solution was boiled for half an hour and cooled. The imide crystallized out in small, yellow blades, which were filtered off, washed free of solvent and dried. Yield, 15 g. or 75% of the theoretical. The crude product was recrystallized several times from xylene using bone black, and finally from glacial acetic, giving 7 g. of bright yellow blades that decompose at about 300° (corr.), but did not melt even at 380° (corr.). The imide is very slightly soluble in boiling benzene, toluene, xylene (1 : 125), and acetic acid (1 : 125). It gives no color when moistened with dimethyl aniline.

Subst. 0.2455, 0.2081. Cc. 0.1 *N* $AgNO_3$; 21.13, 17.96.

Calc. for $C_8HO_2NBr_4$: Br, 69.06. Found: 68.79, 68.98.

Tetrabromophthalanil.—Twenty g. of freshly distilled aniline was added to a boiling solution of 20 g. tetrabromophthalic anhydride in acetic acid. The reaction took place almost at once and the anil precipitated out in gleaming plates. Yield of crude product, 90%. The anil was crystallized from benzene and acetic acid, using bone black until the melting point remained constant. It was finally obtained in almost colorless plates with a faint greenish cast, possibly due entirely to fluorescence. The anil is soluble in benzene, xylene (1 : 40) and acetic acid (1 : 30). It melts at 279.0–280.0° (corr.) and gives a slight orange color with dimethyl aniline.

Subst. 0.2281, 0.2698. Cc. 0.1 *N* $AgNO_3$; 16.99, 20.02.

Calc. for $C_{14}H_5O_2NBr_4$: Br, 59.34. Found: 59.53, 59.30.

Tetrabromophthal-*o*-tolil.—To a solution of 20 g. of anhydride in acetic acid a slight excess of *o*-toluidine was added and the liquid heated to boiling until crystals began to separate. Twenty-two grams, or about 95%. yield were obtained on cooling. The compound was purified from benzene, xylene and acetic acid until the melting point of 291.0–293° (corr.) remained unchanged. The *o*-tolil formed very small, colorless plates, soluble in benzene (1 : 20), xylene (1 : 7) and acetic acid (1 : 100). It gave an orange color with dimethyl aniline.

Subst. 0.2076, 0.2182. Cc. 0.1 *N* $AgNO_3$; 15.05, 15.84.
Calc. for $C_{15}H_7O_2NBr_4$: Br, 57.83. Found: 57.94. 58.02.

Tetrabromophthal-*m*-tolil.—Twenty grams of anhydride was dissolved in 900 cc. acetic acid and a slight excess of *m*-toluidine added. After boiling a few minutes crystals of tolil began to separate as small, almost colorless, glistening plates. The cooled solution gave 23.5 g., or almost theoretical yield. It was purified until a constant melting point of 273.5–274.5° (corr.) was obtained. The tolil dissolves in benzene (1 : 12), xylene (1 : 6), and acetic acid (1 : 70). An orange-red color is produced when the solid is moistened with dimethyl aniline.

Subst. 0.2102, 0.1977. Cc. 0.1 *N* $AgNO_3$; 15.36, 14.35.
Calc. for $C_{15}H_7O_2NBr_4$: Br, 57.83. Found: 58.40, 58.01.

Tetrabromophthal-*p*-tolil.—Fifty grams of anhydride was dissolved in 300 cc. of xylene and a xylene solution containing an excess of *p*-toluidine added. A white, sticky precipitate, probably the toluidine salt of tetrabromophthaltolilic acid, formed immediately. It was filtered off and dissolved in 8000 cc. of boiling acetic acid. The tolil crystallized out on cooling in stringy masses of fine, long, yellow needles. Yield, 47 g., or 80%.

The purified product is very light yellow in color and melts at 280.0–280.5° (corr.). It is soluble in benzene (1 : 20), xylene (1 : 10), and acetic acid (1 : 160). It crystallizes from the first two solvents in well-formed, bright, yellow needles and from acetic acid, acetic anhydride, or ethyl acetate in much lighter yellow needles that are smaller and finer. The bright, yellow needles obtained from xylene were found to lose xylene slowly when heated to 115° for several days. After 3 days the sample came to constant weight, the loss of weight corresponding almost exactly to the ratio of one molecule of xylene to 4 of *p*-tolil.

Subst. 1.7383. Loss 0.0790.
Calc. for $(C_{15}H_7O_2NBr_4)_4.C_6H_4.(CH_3)_2$: Loss 4.58. Found: 4.56.

The crystals obtained from acetic acid did not lose weight at all when heated as above. With dimethyl aniline it gives a red color.

Subst. 0.2060, 0.2033. Cc. 0.1 *N* $AgNO_3$; 14.94, 14.70.
Calc. for $C_{15}H_7O_2NBr_4$: Br, 57.83. Found: 57.96, 57.79.

Tetrabromophthal-*o*-nitroanil.—Twenty grams of anhydride was finely powdered and suspended in 150 cc. of acetic acid. Ten g. of *o*-nitraniline was added and the mixture boiled for 10 minutes. The reaction product was filtered off and gave 14 g., or 56%, crude nitroanil. It was crystallized several times from acetic acid and xylene with bone black to remove the color and finally obtained in very fine, colorless, hair-like crystals melting with decomposition at 289–298.5° (corr.). The *o*-nitroanil is soluble in xylene (1 : 25) and acetic acid (1 : 120). Dimethyl aniline gave a light orange color with the solid nitroanil and an addition product that crystallized as red, stubby quadrilateral plates showing marked dichroic properties.

Subst. 0.2390, 0.2662. Cc. 0.1 *N* $AgNO_3$; 16.44, 18.31.
Calc. for $C_{14}H_4O_4N_2Br_4$: Br, 54.75. Found: 54.97, 54.97.

Tetrabromophthal-*m*-nitroanil.—Twenty grams of anhydride in 900 cc. acetic acid was boiled with 10 g. of *m*-nitraniline until crystals began to form. The cool solution deposited 22 g., or 90%, yield of crude nitroanil in the form of short blades. The purified product from xylene and acetic acid was obtained in slightly cream colored, thin, slender plates, melting at 301.5–303° (corr.). It is soluble in xylene (1 : 80) and acetic acid (1 : 300), giving from the latter solvent straw-colored, slender blades. Dimethylaniline produces a red color.

Subst. 0.2188, 0.2078. Cc. 0.1 *N* $AgNO_3$; 15.07, 14.32.
Calc. for $C_{14}H_4O_4N_2Br_4$: Br, 54.75. Found: 55.05, 55.07.

Tetrabromophthal-*p*-nitroanil.—Ten grams of *p*-nitraniline was added to glacial acetic acid containing 20 g. of anhydride and the solution gently boiled a few minutes. When cool, 10.5 g., or 42%, yield, of crude nitroanil was obtained. Recrystallization from xylene and acetic acid gave long, exceedingly fine, matted clusters of colorless needles that melted at 331–331.5° (corr.). A modification, such as the blades obtained with the corresponding *m*-nitroanil, was observed, but crystals were obtained from xylene as fine, colorless needles arranged in rosets. The solid is colored orange-red when moistened with dimethyl aniline.

Subst. 0.2270, 0.2537. Cc. 0.1 *N* $AgNO_3$; 15.55, 17.33.
Calc. for $C_{14}H_4O_4N_2Br_4$: Br, 54.75. Found: 54.75, 54.59.

Tetrabromophthal-*p*-hydroxyanil.—A slight excess over the calculated amount of *p*-aminophenol was added to an acetic acid solution of the anhydride and boiled for 5 minutes. The desired product was deposited as short, yellow needles. Yield, 95%. It was purified from xylene and acetic acid. The bright, lemon-yellow, stubby needles so obtained melted with decomposition at 296–308° (corr.). The hydroxyanil is soluble in glacial acetic acid (1 : 150) and in xylene (1 : 100), giving from the latter fine, orange needles containing xylene of crystallization. It was found impossible to remove all the xylene of crystallization from the compound by heating alone. Even when heated at 160–190° for several hours some of the orange color of the addition compound persisted. An analysis of the crystals from xylene, after drying in a water oven, showed an addition of one molecule of xylene to 3 of the hydroxyanil.

Subst. 0.2504. Cc. 0.1 *N* $AgNO_3$; 17.16.
Calc. for $(C_{14}H_5O_3NBr_4)_3.C_6H_4(CH_3)_2$: Br, 54.17. Found: 54.19.

A light orange color is produced with dimethyl aniline. Analysis of the compound crystallized from acetic acid gave

Subst. 0.2454, 0.2321. Cc. 0.1 *N* $AgNO_3$; 17.58, 16.62.
Calc. for $C_{14}H_5O_3NBr_4$: Br, 57.62. Found: 57.26, 57.23.

Tetrabromophthal-*p*-acetylaminoanil.—Twenty grams of anhydride was dissolved in acetic acid containing a slight excess of *p*-amino acetanilide and the solution boiled for a few minutes. The product obtained on cooling weighed 23 g., or nearly theoretical. Purification was effected by recrystallization from xylene, acetic anhydride and acetic acid. The compound gave very minute, hair-like, colorless needles which did not melt sharply but decomposed at 381° (corr.). It is rather insoluble in most of the common solvents; xylene (1 : 800), acetic acid (1 : 200), and acetic anhydride (1 : 130). Only a faint yellow color is given with dimethyl aniline.

Subst. 0.2389, 0.2514. Cc. 0.1 *N* $AgNO_3$; 16.06, 16.84.
Calc. for $C_{16}H_8O_3N_2Br_4$: Br, 53.65. Found: 53.73, 53.53.

Tetrabromophthal-*p*-bromoanil.—A slight excess of *p*-bromoaniline was added to a boiling solution of 20 g. anhydride in acetic acid. Crystals soon began to separate, giving 26 g., or 95% yield, on cooling. Purified in the usual way the derivative was obtained in the form of minute, narrow blades, tinged with a very faint greenish color. It did not melt when heated to 380° (corr.). The *p*-bromoanil is slightly soluble in xylene (1 : 350), benzene (1 : 650), and nearly insoluble in acetic acid or anhydride and ethyl acetate.

Subst. 0.2921, 0.2265. Cc. 0.1 *N* $AgNO_3$; 23.60, 18.36.
Calc. for $C_{14}H_4O_2NBr_5$: Br. 64.69. Found: 64.57, 64.78.

Tetrabromophthal-2,4-dibromoanil.—Twenty grams of anhydride was dissolved in acetic acid, 14 g. of 2,4-dibromoaniline added, and the solution boiled for 15 minutes. Upon cooling, 30 g., or a theoretical yield of crude product, was obtained, which was purified as usual. It gave exceedingly small, colorless prisms that melted at 296–298.5° (corr.). One g. of anil dissolves in 200 cc. of acetic acid or 50 cc. of xylene. Dimethyl aniline colors it an orange-red.

Subst. 0.2376, 0.2181. Cc. 0.1 *N* $AgNO_3$; 20.40, 18.80.
Calc. for $C_{14}H_3O_2NBr_6$: Br, 68.85. Found: 68.62, 68.89.

Tetrabromophthal-2,6-dibromoanil.—In this case the usual condensation cannot be carried out in glacial acetic acid. This may be due either to steric hindrance caused by bromine occupying the two ortho positions in the aniline molecule, or more probably to the decreased alkaline reaction of the molecule which prevents opening the lactone ring for the first step in the reaction. Thirty g. of powdered anhydride and 20 g. of 2,6-dibromoaniline were thoroughly mixed with 5 g. of freshly fused zinc chloride and heated in an oil bath at 150–160° for two hours. The mixture softened somewhat, forming a gummy purple melt that was extracted with alcohol until the color was largely removed. It was then boiled up with 3 liters of acetic acid. Cooling gave 22.5 g., or about 50% yield. The pure anil from xylene gave nearly colorless hexagonal crystals that melted at 323.5–327° (corr.). It is soluble in xylene (1 : 35) and acetic acid (1 : 200). With dimethyl aniline a faint yellow color was noted.

Subst. 0.3824, 0.2257. Cc. 0.1 *N* $AgNO_3$; 32.95, 19.58.
Calc. for $C_{14}H_3O_2NBr_6$: Br, 68.84. Found: 68.87, 69.33.

Tetrabromophthal-2,4,6-tribromoanil.—An intimate mixture of 30 g. anhydride, 23 g. of 2,4,6-tribromoaniline, and 3 g. zinc chloride was heated at 180–200° for two hours. The purple mass was extracted with alcohol, leaving 30.5 g., or 60%, yield. The crude anil was recrystallized from acetic acid and benzene-alcohol, giving colorless diamond-shaped plates, melting at 297–298° (corr.). The compound is quite soluble in benzene, xylene and acetic acid (1 : 30), slightly so in alcohol. Dimethyl aniline gave a light orange color.

Subst. 0.2224, 0.2064. Cc. 0.1 *N* $AgNO_3$; 20.06, 18.74.
Calc. for $C_{14}H_2O_2NBr_7$; Br, 72.14. Found: 72.09, 72.56.

Tetrabromophthal-*p*-iodoanil.—Twenty grams of anhydride and 12 g. *p*-iodoaniline in acetic acid were boiled for a few minutes until the crystallization began. The solution deposited, on cooling, 27.5 g., or 70%, yield. Purification by repeated crystallization from xylene gave short, stubby blades which decomposed without melting, about 381° (corr.). The color of the anil is bright yellow with a faint greenish tinge. It is only slightly soluble in benzene, alcohol, xylene (1 : 150), less so in acetic acid.

Subst. 0.2479, 0.2438. Cc. 0.1 *N* $AgNO_3$; 18.67, 18.37. Weight of AgBr + AgI; 0.3692, 0.3610.

Calc. for $C_{14}H_4O_2NBr_4I$: Br, 48.09; I, 19.10. Found: Br, 47.09, 48.23; I, 20.21, 18.91.

Tetrabromophthal-3,4-dimethylanil.—Condensation in acetic acid of 20 g. of anhydride with 1,3,4-xylidine (Kahlbaum's) gave 21 g., or 90%, yield of crude product that was recrystallized from ethyl acetate and acetic acid. The colorless plates so obtained melted at 264.5–271° (corr.). The dimethylanil is very soluble in xylene, benzene, chloroform and carbon tetrachloride, less so in ethyl acetate, acetone, and ligroin, and only slightly in acetic acid. With dimethyl aniline an orange color is given.

Subst. 0.2025, 0.2152. Cc. 0.1 *N* $AgNO_3$; 14.28, 15.23.
Calc. for $C_{16}H_9O_2NBr_4$: Br, 56.38. Found: 56.36, 56.56.

Tetrabromophthal-2,4,5-trimethylanil.—A solution of 20 g. anhydride containing an excess of pseudo-cumidine was boiled for a few minutes. On cooling there was recovered 25 g. or a theoretical yield of small, flat, colorless crystals. The product was recrystallized from benzene and xylene by the addition of alcohol, giving diamond-shaped crystals, colorless except for a faint greenish cast, that melted at 307–308° (corr.). The trimethylanil is soluble in benzene (1 : 40), xylene (1 : 15), fairly soluble in acetic anhydride and insoluble in alcohol. No color is given with dimethyl aniline.

Subst. 0.2087, 0.2910. Cc. 0.1 *N* $AgNO_3$; 14.42, 19.99.
Calc. for $C_{17}H_{11}O_2NBr_4$: Br, 55.03. Found: 55.16, 54.82.

Tetrabromophthal-*o*-carboxyanil.—The carboxylic acid derivative of tetrabromophthalanil was prepared to study the influence of an acid group in the aniline residue both as regards condensation with anhydride and especially in connection with its proximity effects on the molecule as a whole. Anthranilic acid condensed readily with anhydride in the usual way, but it was necessary to distill off about half the solvent before crystallization of the resulting anil took place. The yield was almost theoretical. Crystallized from xylene and acetic acid, it was obtained as colorless prims melting at 315.5–316.5° (corr.). The carboxyanil dissolves in acetic acid (1 : 80), xylene (1 : 120) and in dilute sodium hydroxide solution with salt formation, but without color. Hydrochloric acid precipitates unchanged anil from a solution of its salt. With dimethyl aniline a bright yellow color is given.

Subst. 0.2411, 0.2835. Cc. 0.1 *N* $AgNO_3$; 16.49, 19.34.
Calc. for $C_{15}H_5O_4NBr_4$: Br, 54.85. Found: 54.66, 54.52.

Tetrabromophthal-*o*-ethoxyanil.—A slight excess of *o*-phenetidine was added to an acetic acid solution of 20 g. anhydride and boiled for a few minutes. Twenty-four g., or a theoretical yield of small, well-formed plates was obtained on cooling. Purification was effected from benzene and xylene solutions by the addition of alcohol as the product is very soluble in these solvents, and nearly insoluble in alcohol. It forms small, iridescent, light yellow plates, melting at 247–248° (corr.). A slight orange color is given by dimethyl aniline.

Subst. 0.2794, 0.2730. Cc. 0.1 *N* $AgNO_3$; 19.15, 18.94.
Calc. for $C_{16}H_9O_3NBr_4$: Br, 54.85. Found: 54.72, 55.38.

Tetrabromophthal-*p*-ethoxyanil.—The para derivative was made similarly to the above from anhydride and *p*-phenetidine. A 92% yield of long, silky crystals was obtained. The crude material purified in the same way and finally recrystallized from acetic anhydride, gave cotton-like masses of light yellow filamentous crystals melting at 272.5–273° (corr.). It is soluble in acetic anhydride (1 : 15), xylene (1 : 20), benzene (1 : 40), and phenol; insoluble in alcohol, acetone and ethyl acetate. Dimethyl aniline gave a slight orange color.

It is interesting to note that the *o*-ethoxyanil was obtained in the plate formation while the corresponding *p*-ethoxy derivative gave only cotton-like needles. There is little doubt but that we have here another case of dimorphism[1] similar to that observed with tetrachlorophthal-*p*-tolil.

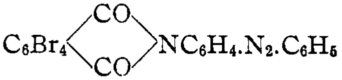
Subst. 0.2434, 0.2274. Cc. 0.1 *N* $AgNO_3$; 16.68, 15.68.
Calc. for $C_{16}H_9O_3NBr_4$: Br, 54.85. Found: 54.71, 55.04.

Tetrabromophthal-α-naphthylimide.—A slight excess of α-naphthylamine was added to 20 g. of anhydride in acetic acid, the solution boiled for a few minutes and cooled. Twenty-five g., representing nearly a theoretical yield of the imide, was obtained. The purified product from benzene and xylene formed light yellow needles, melting at 309–309.5° (corr.). It is soluble in xylene (1 : 60), benzene (1 : 70), and acetic acid (1 : 400). With dimethyl aniline an orange-red color is produced.

Subst. 0.2071, 0.1989. Cc. 0.1 *N* $AgNO_3$; 14.11, 13.58.
Calc. for $C_{18}H_7O_2NBr_4$: Br, 54.29. Found: 54.45, 54.57.

Tetrabromophthal-β-naphthylimide.—The β-naphthylimide was prepared in a similar way giving a practically theoretical yield. The pure substance formed very light greenish yellow plates that melted at 305.5–308° (corr.). It is soluble in xylene (1 : 40), benzene (1 : 90), and acetic acid (1 : 500). A similar light orange color is produced with dimethyl aniline.

Subst. 0.2691, 0.2479. Cc. 0.1 *N* $AgNO_3$; 18.28, 16.86.
Calc. for $C_{18}H_7O_2NBr_4$: Br, 54.29. Found: 54.29, 54.48.

Tetrabromophthal-*p*-aminoazobenzene,  $C_6Br_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle NC_6H_4.N_2.C_6H_5$ (*p*).—An acetic acid solution containing 10 g. of *p*-aminoazobenzene was added to a boiling solution of anhydride. After a few minutes' heating crystals began to form. The cooled solution deposited 26.5 g., or 95%, yield of crude product that was recrystallized several times from xylene and acetic acid. Thin, orange plates were obtained, melting at 328.5–330° (corr.). It is very slightly soluble in acetic acid or anhydride, benzene and ethyl acetate, readily in xylene and nitrobenzene.

Subst. 0.3052, 0.2482. Cc. 0.1 *N* $AgNO_3$; 18.89, 15.30.
Calc. for $C_{20}H_9O_2N_3Br_4$: Br, 49.73. Found: 49.47, 49.27.

Tetrabromophthal-semicarbazone.—The semicarbazone was made by adding 6 g. of semicarbazide hydrochloride and an equivalent amount of fused sodium acetate to a boiling acetic acid solution of anhydride. After 5 minutes' heating a white precipitate began to form. Yield, 20 g., or 85% theoretical. The crude product was recrystallized from nitrobenzene, acetic acid, and finally by dissolving several times in melted

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[1] THIS JOURNAL, 40, 208 (1918).

phenol from which it was thrown out by alcohol. It crystallized, when pure, in short, stubby prisms showing a faint greenish tinge. The melting point was not obtainable as the semicarbazone turns red at 100° with decomposition. No color was given with dimethyl aniline.

Subst. 0.2260, 0.3083. Cc. 0.1 *N* $AgNO_3$; 17.17, 23.44.
Calc. for $C_9H_5O_3N_3Br_4$: Br, 60.23. Found: 60.65, 60.70.

Tetrabromophthal-phenylhydrazone.—A slight excess of phenylhydrazine was added to a boiling acetic acid solution containing 20 g. of anhydride. Crystals separated after a few minutes' boiling. Yield, 23 g., or theoretical. Recrystallization from xylene and acetic anhydride gave light orange blades melting at 314–317.5° (corr.). The hydrazone is soluble in xylene (1 : 100), acetic anhydride (1 : 100), slightly in benzene, ethyl acetate, acetone and acetic acid (1 : 400).

Subst. 0.2421, 0.2382. Cc. 0.1 *N* $AgNO_3$; 17.50, 17.23.
Calc. for $C_{14}H_6O_2N_2Br_4$: Br, 57.72. Found: 57.71, 57.75.

Tetrabromophthal - ethylphenylhydrazone. —Tetrabromophthal-ethylphenylhydrazone was made by adding a slight excess of ethylphenylhydrazine to a boiling acetic acid solution of tetrabromophthalic anhydride. Upon cooling the hydrazone separated as bright *red* needles. Purification was effected by repeated crystallization from benzene and acetic acid until a product was obtained which melted at 211.0–211.5° (corr.).

The ethylphenylhydrazone crystallizes from benzene, ethyl acetate and xylene as bright *yellow* needles. Upon heating, these change to red at 95–96°, and then melt at the same temperature as the red variety. Heating a sample of yellow crystals from benzene to 110° occasioned a loss in weight equal to one molecule of solvent. If the red variety be kept in a desiccator over benzene it gradually turns yellow and increases in weight to the extent of about two-thirds of a molecule of benzene. Over conc. sulfuric acid *in vacuo*, loss of weight occurs and change in color from yellow to red.

Subst. 0.7802. Loss 0.0921.
Calc. for $C_{16}H_{10}O_2N_2Br_4.C_6H_6$: Loss, 11.83. Found: 11.78.

The purified compound obtained from acetic acid was analyzed.

Subst. 0.2360, 0.2042. Cc. 0.1 *N* $AgNO_3$; 16.50, 14.02.
Calc. for $C_{16}H_{10}O_2N_2Br_4$: Br, 54.94. Found: 55.28, 54.29.

Tetrabromophthal-2,4,6-tribromophenylhydrazone.—A slight excess of 2,4,6-tribromophenylhydrazine was added to a boiling acetic acid solution of 20 g. of tetrabromophthalic anhydride. Condensation took place immediately and the tribromophenyl hydrazone separated as very fine, hair-like needles. The yield, after filtering and washing, was 34 g., or very nearly theoretical. The compound was purified by repeated crystallization from benzene, acetic anhydride, xylene and glacial acetic acid until no change in the melting point of 290–291° (corr.) was obtained. Even after this extensive purification no very satisfactory analyses could be obtained. The 2,4,6-tribromophenylhydrazine itself loses bromine on standing and it is probable that the hydrazone is also unstable.

Tetrabromophthal-2,4,6-tribromophenylhydrazone is very soluble in pyridine, and somewhat less so in xylene (1 : 50), acetic anhydride (1 : 140), benzene (1 : 100), acetic acid (1 : 400), and acetone. It is insoluble in alcohol and ethyl acetate. It crystallizes in very long, thin needles, resembling cotton batton, possessing a light greenish yellow color. With dimethylaniline a slightly orange color is produced.

Subst. 0.3329, 0.2511. Cc. 0.1 *N* $AgNO_3$; 29.27, 22.23.
Calc. for $C_{14}H_8O_2N_2Br_7$: Br, 70.77. Found: 69.52, 70.00.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES, CONSTITUTION AND COLOR, XV.[1] 3,4,6-TRIIODOPHTHALOXIME AND SOME OF ITS DERIVATIVES.

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Tetraiodophthaloxime failed to give instances of the dimorphism which had been observed with various derivatives of the corresponding tetrachlorophthaloxime.[2] This property of appearing in two distinct crystal forms, one stable, the other unstable at ordinary temperatures, has been found quite characteristic of many substituted phthalimide derivatives. Inasmuch as both phthaloxime itself and tetraiodophthaloxime gave no examples of dimorphism while tetrachlorophthaloxime appeared to be especially adapted constitutionally to show this property, it was thought desirable to prepare the triiodophthaloxime series. The 3 atoms of iodine might correspond in effect to 4 of chlorine in so far as any proximity effects were concerned. It was also desirable to have this new series of substituted phthalic acid derivatives for spectroscopic study.

3,4,6-Triiodophthaloxime.—The triiodophthalic anhydride necessary was prepared and purified following the recent methods of Pratt and Perkins.[3] Fifty grams of the yellow crystals were finely powdered and suspended in about 400 cc. of water containing 10 g. of hydroxylamine hydrochloride and 12.1 g. of sodium bicarbonate. The mixture was placed in a briskly boiling water bath and frequently stirred. It

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[1] THIS JOURNAL, 40, 412 (1918).

[2] *Ibid.*, 40, 407 (1918).

[3] *Ibid.*, 40, 219 (1918).