dissolved in 100 cc. carbon tetrachloride and a small crystal of iodine was added. The flask, fitted by ground joint to a reflux condenser, was placed on an electric hot plate in direct sunlight and the contents allowed to boil. 11.7 g. (1 mol) bromine dissolved in 50 cc. carbon tetrachloride were introduced in small quantities at a time by means of a separatory funnel whose stem was sealed into the side of the lower part of the condenser tube. Rapid evolution of hydrogen bromide began at once. This was absorbed by water contained in Folin bulbs fitted to the upper end of the condenser.[1] When all the bromine had been used up the flask was detached after cooling and the carbon tetrachloride distilled off. On cooling, the oily residue at the botton of the flask crystallized in a solid mass. This was dissolved by boiling in 95% alcohol and filtered. The filtrate was rapidly cooled and allowed to stand a short time at 0°. The fine crystals were filtered by suction and dried in the air overnight. The yield was 11.2 grams, or 71% of the theoretical. Melting point 99–100°, uncorrected.

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PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR. XII.[2] TETRACHLOROPHTHALOXIME AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND CHARLOTTE H. MILLER.

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The study of phthalic acid derivatives resulting from replacement in various positions in the molecule and the effects thereby on color has been continued. The present paper considers certain derivatives of tetrachlorophthalic anhydride obtained after one oxygen atom has been replaced by the NOH radical. The reaction is brought about readily by treating tetrachlorophthalic anhydride with an aqueous solution of hydroxylamine. The particular interest in the resulting oxime lies in the proximity effects taking place between the hydroxyl group and the nucleus. This effect becomes very marked on salt formation when it is evidenced to the eye by a vivid red color.

Unhalogenated phthaloxime was found to exist in two modifications, one colorless, and the other canary yellow,[3] but neither Orndorff and

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[1] The apparatus can be simplified by covering the carbon tetrachloride solution in the flask with a little water. This absorbs all hydrogen bromide. If the bromide is introduced by a separatory funnel the tip of whose stem extends down the condenser tube to the point where the vapors condense, there is no loss of bromine whatever and the experiment can be conducted in the open laboratory. The yields by this method are somewhat lower.

[2] THIS JOURNAL, **40**, 254 (1918).

[3] Orndorff and Pratt, *Am. Chem. J.*, **47**, 90 (1912).

Nichols,[1] who first prepared the tetrachloro derivative, nor the authors, have observed a similar phenomenon in this case. We have made the oxime under a variety of conditions but always obtained a pale yellow form.

The oxime readily yields a red silver salt from which a variety of ethers were prepared. It should be noted that whereas the oxime itself is faintly yellow the derivatives are all without color. Yellow phthaloxime did give yellow compounds throughout the series as far as developed and such would be expected from the tetrachloro-oxime if it corresponded to the colored isomer. The colorless ethers here reported lead us to believe that the tetrachloro-phthaloxime itself, although yellow, corresponds to the colorless phthaloxime, and that the higher colored form has not yet been obtained.

The new derivatives here reported did show, however, new and interesting cases of dimorphism which establish their position in relation to the anil derivatives already discussed.[2] These anils result from a series of steps in the type reaction between phthalic anhydride and primary aromatic amines and are considered as derived from phthalimide by the replacement of hydrogen by phenyl, etc., whereas in the oxime this hydrogen is replaced by hydroxyl. Dimorphism in phthaloxime derivatives had not been observed before, and even in these tetrachloro compounds it was not always possible to obtain two forms. In many cases, however, an individual product could be isolated both as long cotton-like needles and as compact stubby prisms, each form readily convertible into the other.

The methyl ether from silver salt and methyl iodide could be obtained only in the form of compact colorless blades, but the corresponding ethyl ether shows very distinctly this unusual property. When a saturated solution in methyl alcohol is cooled rapidly the ether crystallizes out readily in exceedingly fine hair-like clusters resembling wisps of cotton. These crystals, on standing some hours in the mother liquor, go over gradually into colorless, thick prisms so entirely distinct as to suggest a different substance. Both forms have the same melting point or very nearly so, and show no different mixed melting point.

The isopropyl ether exists both as very thin, gleaming plates and as heavy prisms. The benzyl ether could be obtained only as cotton-like wisps, while the benzoate gave nacreous diamond-shaped plates and prisms. Similarly, the allyl ether gave both coarse prisms and fine needles.

This property of dimorphism appears to be particularly favored by the presence of the four chlorine atoms in the molecule. It has never been observed in the phthaloxime series and was not found with correspond-

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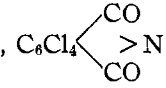
[1] *Am. Chem. J.*, 48, 495 (1912).

[2] THIS JOURNAL, 40, 203 (1918).

ing tetraiodo compounds. In all cases where two forms were obtained there appeared to be no other differences with the possible exception of melting points. These sometimes appeared to differ slightly but rapid conversion of the less stable into the more stable form near the melting point made analytical differentiation impossible.

The easy conversion of one form into the other without change in weight, often so rapidly that the transformation could be followed under the microscope, leads us to consider the phenomenon one of dimorphism probably due to different arrangements of identical molecules in the crystals. The dimorphism, therefore, is entirely analogous to that reported for tetrachlorophthal-*p*-tolil *q. v.*

Tetrachlorophthalyl phenylhydrazone was prepared from anhydride and phenylhydrazine for purposes of comparison. As ordinarily obtained either from glacial acetic acid or alcohol, it forms long, curving, orange needles tending to cluster in sheaves. It was observed on examining these crystals under the microscope that very rapid cooling of the acetic acid solution gave thin four-sided lemon-yellow plates if fairly large size. These plates show interference colors as they float in the mother liquor and could not be confused with the orange needles. The plates go over into the stable needles instantly when moistened with alcohol. It was not possible to obtain the unstable form free from the needles, as the same change takes place even in the dry crystals.

The dimorphism here is analogous to that observed by Dunlap[1] and studied by Chattaway.[2] Both forms probably have the symmetrical structure,  $C_6Cl_4\left\langle\genfrac{}{}{0pt}{}{CO}{CO}\right\rangle N.NHC_6H_5$ and are to be considered as derived from the oxime by the replacement of hydroxyl by the anilino group.

The various new derivatives here reported will be considered from the theoretical standpoint of constitution and color when necessary absorption spectra apparatus becomes available.

Experimental.

Tetrachlorophthaloxime.—57.0 g. of tetrachlorophthalic anhydride were ground to pass an 80-mesh sieve, an important factor in securing good yields as otherwise considerable amounts of material remain unacted upon. 17.4 g. of hydroxylamine hydrochloride and 17.3 g. of sodium carbonate were dissolved in 200 cc. of water and the finely ground anhydride added. The suspension was stirred about ten minutes at room temperature, then placed in a bath of boiling water for 4 hours. It was stirred occasionally during the heating, finely acidified with dilute hydrochloric acid and filtered. The product was washed with hot water until

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[1] THIS JOURNAL, **27**, 1091 (1905).

[2] *J. Chem. Soc.*, **99**, 2253 (1911).

free from acid. Yield, 57 g. or 95% theoretical. The hydrate so obtained was recrystallized from methyl alcohol and acetone, dried to constant weight at 120° and analyzed.

Subst. (I) 0.1350, (II) 0.1227; cc. 0.1 *N* $AgNO_3$, (I) 18.03, (II) 16.34.
Calc. for $C_8HO_3NCl_4$: Cl, 47.14%. Found: (I) 47.38, (II) 47.22.

Chlorine was determined by the lime combustion method.

Silver Salt of Tetrachlorophthaloxime.—The silver salt was prepared by dissolving the oxime in boiling methyl alcohol and adding a solution containing four equivalents of silver nitrate in water and just enough ammonia to redissolve the silver oxide. The silver salt precipitated as a gelatinous, red mass, It was warmed 15 minutes on a water bath to insure complete reaction, filtered and washed free from excess silver with methyl alcohol. Yield, theoretical. It was not possible to remove all adsorbed silver nitrate as shown by analysis. This was made by treating a sample of the dry salt with dilute nitric acid in the cold, letting it stand overnight, and titrating the silver nitrate so formed with standard ammonium thiocyanate.

Subst. (I) 0.1561, (II) 0.1321; cc. 0.1 *N* NH_4SCN, (I) 4.43, (II) 3.84.
Calc. for $C_8O_3NCl_4Ag$: Ag, 26.46%. Found: (I) 30.66, (II) 31.36.

Methyl Ether—5.0 g. of dry silver salt were suspended in ether containing 3 cc. of methyl iodide and boiled gently with a reflux condenser for 48 hours. The ether was recrystallized from alcohol in the form of shining, colorless blades, melting at 206° (corr.). No other form was observed.

Subst. (I) 0.0493, (II) 0.0896; cc. 0.1 *N* $AgNO_3$, (I) 6.25, (II) 11.32.
Calc. for $C_9H_3O_3NCl_4$: Cl, 45.04%. Found: (I) 44.95, (II) 44.80.

Ethyl Ether.—The ethyl ether similarly made was recrystallized from ether by adding ligroin, followed by slow distillation. It was thus obtained as coarse, colorless prisms, generally in star-like clusters and melting at 160° (corr.). The ethyl ether dissolves readily in boiling methyl or ethyl alcohol, and deposits, on rapid cooling, in abundant, fine, hair-like crystals which mat together like cotton. Brief standing in the mother liquor converts this unstable form into prisms, but it is quite stable when dry.

Subst. (I) 0.0929, (II) 0.1168; cc. 0.1 *N* $AgNO_3$, (I) 11.26, (II) 14.27.
Calc. for $C_{10}H_5O_3NCl_4$: Cl, 43.12%. Found: (I) 43.06, (II) 43.32.

Isopropyl Ether.—The isopropyl ether was extracted from resulting silver iodide with boiling chloroform in which it is very soluble. Methyl alcohol was then added slowly to abundant crystallization. The isopropyl ether forms either very thin, glistening plates or clusters of coarse prisms, the latter apparently being the stable form. Both modifications are colorless and melt at 146° (corr.).

Subst. (I) 0.0934, (II) 0.0997; cc. 0.1 *N* $AgNO_3$. (I) 10.89, (II) 11.70.
Calc. for $C_{11}H_7O_3NCl_4$: Cl, 41.35%. Found: (I) 41.34, (II) 41.61.

Isoamyl Ether.—Recrystallized from chloroform-alcohol mixture by sudden cooling it forms fine hair-like crystals which go over into the short prism form on standing. It melts at 244° (corr.).

Subst. (I) 0.0852, (II) 0.0587; cc. 0.1 *N* $AgNO_3$. (I) 9.18, (II) 5.99.
Calc. for $C_{13}H_{11}O_3NCl_4$: Cl, 38.23%. Found: (I) 38.21, (II) 38.84.

Allyl Ether.—The allyl ether was prepared from freshly distilled allyl iodide and silver salt suspended in ether and boiled 7 hours. The solvent was distilled off and the residue extracted with boiling chloroform. The product was recrystallized from chloroform and glacial acetic acid. Rapid cooling of the solution sometimes gave the hair-like form, but as a rule clusters of short, stubby prisms were obtained. They are without color and melt at 186° (corr.).

Subst. (I) 0.1138, (II) 0.1048; cc. 0.1 *N* $AgNO_3$. (I) 13.27, (II) 12.38.
Calc. for $C_{11}H_5O_3NCl_4$: Cl, 41.60%. Found: (I) 41.50, (II) 41.89.

Benzyl Ether.—The benzyl ether was made by boiling the silver salt with an excess of benzyl chloride until the red color disappeared. The solution was then filtered hot and alcohol added to precipitation. The substance was recrystallized from acetone and alcohol. It was obtained only in the colorless cotton-like form, melting at 192° (corr.).

Subst. (I) 0.1455, (II) 0.1337; cc. 0.1 *N* $AgNO_3$. (I) 14.07, (II) 13.68.
Calc. for $C_{15}H_7O_3NCl_4$: Cl, 36.27%. Found: (I) 36.48, (II) 36.29.

Acetate.—5.0 g. of tetrachlorophthaloxime and 10 cc. of acetic anhydride were boiled gently until dissolved, cooled and poured into about 30 cc. of absolute alcohol. The acetate was filtered off, washed with alcohol, and recrystallized from ethyl ether. Yield, practically quantitative. The substance was obtained only in colorless needles melting at 179.5° (corr.). Nitrogen was determined by the Kjeldahl method after thorough reduction with zinc dust and dilute sulfuric acid.

Subst. (I) 0.1148, (II) 0.1069; cc. 0.1 *N* $AgNO_3$. (I) 13.40, (II) 12.55.
Calc. for $C_{10}H_3O_4NCl_4$: Cl, 41.36%. Found: (I) 41.39, (II) 41.60.

Subst. (III) 0.2212, (IV) 0.2433; cc. 0.1 *N* HCl. (III) 6.56, (IV) 7.11.
Calc. for $C_{10}H_3O_4NCl_4$: N, 4.08%. Found: (III) 4.16, (IV) 4.09.

Benzoate.—5.0 g. of silver salt suspended in ether were treated at room temperature with 5 cc. of benzoyl chloride. The reaction takes place at once with the evolution of considerable heat. The solvent was distilled off and excess benzoyl chloride removed by boiling the residue with methyl alcohol. The benzoate, in about 80% yield, was recrystallized by rapid cooling from chloroform as pearly four-sided diamond plates. When the plates are moistened with methyl alcohol they are converted into stubby prisms. The change takes with sufficient rapidity to show clearly under the microscope. Both forms are colorless and melt at 210° (corr.).

Subst. (I) 0.1705, (II) 0.1000; cc. 0.1 *N* $AgNO_3$. (I) 16.87, (II) 9.88.
Calc. for $C_{15}H_5O_4NCl_4$: Cl, 35.02%. Found: (I) 35.08, (II) 35.04.

Tetrachlorophthalyl Phenyl Hydrazone.—5.0 g. of tetrachlorophthalic anhydride in 200 cc. glacial acetic acid were added to 2 cc. of phenylhydrazine in 25 cc. of the same solvent and the mixture boiled for 15 minutes. The first reaction is the formation of anilino-tetrachloro-phthalamic acid, but this readily splits off a molecule of water during the heating and gives orange needles of the phenylhydrazone. The product was recrystallized from glacial acetic acid and from alcohol. The yellow plate modification was obtained by very rapid cooling of an acetic acid solution. It is unstable and rapidly reverts to the orange needles. The substance melts at 287° (corr.).

Subst. (I) 0.0793, (II) 0.0977; cc. 0.1 *N* $AgNO_3$. (I) 8.23, (II) 10.37.
Calc. for $C_{14}H_6O_2N_2Cl_4$: Cl, 37.73%. Found: (I) 37.75, (II) 37.64.

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PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR. XIII.[1] TETRAIODOPHTHALOXIME AND SOME OF ITS DERIVATIVES.

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The large proportion of iodine in tetraiodophthalic anhydride and its sulfur yellow color, probably due to the proximity effects of the unsaturated halogen atoms, made it desirable to prepare the corresponding oxime. The study of substituted phthalic acid compounds was, therefore, made to include the material reported in this paper. Tetraiodophthalic anhydride represents the maximum molecular weight possible in a halogenated ring, the presence of the most unsaturated halogen atoms, and the greatest effect obtainable by this type of substitution.

Tetraiodophthaloxime was obtained without difficulty. 50.0 g. of tetraiodophthalic anhydride,[2] ground to a fine powder, were added to a solution of 6.4 g. hydroxylamine sulfate and 6.6 g. sodium bicarbonate in 250 cc. water. The suspension was warmed in a boiling water bath for 2 hours with occasional stirring, finally acidified with hydrochloric acid to break up any oxime salt, and filtered. The product was washed thoroughly with hot water until free from inorganic matter and dried. Yield, 52.0 g. crude oxime or 93% theoretical.

The impure product was recrystallized until pure from glacial acetic

[1] THIS JOURNAL, **40**, 407 (1918).

[2] Pratt and Shupp, *Ibid.*, 40, 254 (1918).