Determination of the Index of Refraction.—The index of refraction of trimethylene oxide was determined by the Abbé refractometer using ordinary (white) light. The following readings were taken:

$N^{24°}$.... 1.3900, 1.3895, 1.3899, 1.3899, 1.3897, 1.3892, 1.3901, 1.3895, 1.3898, 1.3899.

Determination of the Molecular Weight.—The molecular weight of trimethylene oxide was determined by the method of Victor Meyer. Three determinations were made with the following results: 61.5; 56.8; 55.5. The calculated molecular weight is 58.

Residues from the Preparation of Trimethylene Oxide (Chlorohydrin Method).—After the trimethylene oxide had been driven from the generating flask, the residues were cooled and the water solutions extracted with ether. The ether solution was dried over anhydrous sodium sulfate, and the ether distilled over. The residue was subjected to fractional distillation. A considerable quantity of the liquid distilled over below 100°. This portion was treated with bromine and found to add that substance quantitatively. From 100 to 150° little distilled over, but from 150 to 190° there was an increased quantity of distillate. It was this portion that Reboul considered to be the unchanged chlorohydrin. But it was found that this fraction also reacted vigorously and completely with bromine to form heavy oils, while the chlorohydrin under similar conditions will not react at all. From 200° under ordinary pressure to 270° under 30 mm. several fractions were obtained, all of which formed heavy bromides with bromine. The latter fractions were viscous oils which seemed to have minute crystals in the liquid. However, they did not crystallize further on standing for three months.

URBANA, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THE NITRATION PRODUCTS OF PHENOLTETRACHLOROPHTHALEIN AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND J. J. KENNEDY.

Received September 8, 1916.

The investigation of the nitration products of phenoltetrachlorophthalein and their derivatives was undertaken to study the effect of introducing negative groups into the phthalein molecule.

The phenol used in this investigation was a pure crystallized product. This was distilled, the first fraction being rejected, and only that distilling between 180° and 181° was used. This product was perfectly colorless and melted sharply at 42°. Commercial tetrachlorophthalic acid was purified by the method described by Delbridge.[1] The purity of the acid

---

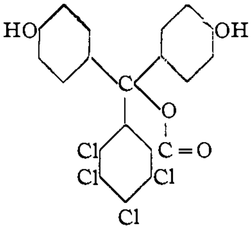
[1] *Am. Chem. J.*, 41, 414 (1909).

used was checked by determining its molecular weight by titration[1] with standard alkali.

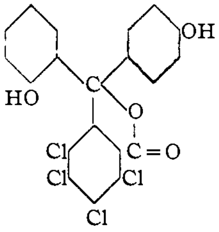
Phenoltetrachlorophthalein.—This compound was made by the method of Orndorff and Black,[2] the only difference being that tetrachlorophthalic acid was used instead of the corresponding amount of tetrachlorophthalic anhydride. The yield of the phthalein was the same and the same amount of tetrachlorofluoran was formed. The pure phenoltetrachlorophthalein[3] was found to melt[4] sharply at 316–317°, with decomposition. The product, dried in an electric oven[5] at 120°, gave the following results on analysis:[6]

Subst., I, 0.2249; II, 0.2021; cc. 0.1 *N* $AgNO_3$, I, 19.78; II, 17.71.
Calc. for $C_{20}H_{10}Cl_4O_4$: Cl, 31.11%. Found: I, 31.19; II, 31.07.

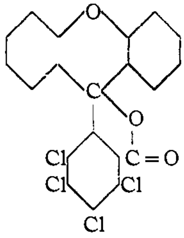
Phenoltetrachlorophthalein Dibenzoate.—This compound was not made by Orndorff and Black. It was prepared to determine if the phenoltetrachlorophthalein was not a mixture of two isomers. According to theory, three products are possible in the condensation of phenol with tetrachlorophthalic acid.



(I).



(II).



(III).

The compound represented by Formula III is tetrachlorofluoran, easily separated from the phthalein, owing to its insolubility in aqueous alkali. The greater amount of the product formed probably has the structure represented by Formula I in which the methane carbon atom is in the para position to each of the hydroxyl groups. However, the compound, represented by Formula II, in which one hydroxyl is ortho and the other para to the methane carbon atom, presents another possibility. If phenoltetrachlorophthalein is a mixture of these two phthaleins, then two dibenzoates should be formed. With this idea in view, the

---

[1] *Am. Chem. J.*, **41**, 399 (1909).

[2] *Ibid.*, **41**, 360 (1909).

[3] Phenoltetrachlorophthalein is described by Orndorff and Black as not melting at 300°.

[4] All melting points described in this article are uncorrected and were determined with carefully standardized thermometers using an electrically heated Thiele apparatus.

[5] *Am. Chem. J.*, **48**, 477 (1912).

[6] All the chlorine determinations were made by the lime method. *Am. Chem. J.*, **41**, 393 (1909). International atomic weights for 1916 are used in this article.

benzoyl derivative of phenoltetrachlorophthalein was made and carefully studied. Ten grams of phenoltetrachlorophthalein were heated to boiling with 70 g. of pure benzoyl chloride when all the phthalein went into solution. The boiling was continued for ten minutes and the contents of the flask poured into alcohol. The benzoate, after repeated washing with boiling water, was obtained in a nearly colorless, amorphous condition. It was then boiled with 95% alcohol, to remove the last traces of benzoyl chloride. The yield was practically quantitative, 98% of the calculated amount being obtained. The benzoate was crystallized several times from a *boiling* mixture of acetone and ethyl alcohol and obtained as a colorless, crystalline product, melting at 213°. Analyses showed that this product, was the pure anhydrous dibenzoate. On heating for an hour at 120° there was no loss in weight.

Subst., I, 0.2052; II, 0.2304; cc. 0.1 *N* $AgNO_3$, I, 12.37; II, 13.85.
Calc. for $C_{34}H_{18}O_6Cl_4$: Cl, 21.36%. Found: I, 21.38; II, 21.31.

Some of the product melting at 213° was then recrystallized from a mixture of acetone and ethyl alcohol *in the cold.* It now appeared in the form of flocks melting at about 165°. Another portion of the anhydrous material recrystallized slowly from benzene in the cold was obtained in white flocks, melting at about 155°. The compound from benzene lost a molecule of water,

Subst., I, 0.3144; II, 0.4235, loss (water) at 130°; I, 0.0074; II, 0.0102.
Calc. for $C_{34}H_{18}O_6Cl_4$: H_2O, 2.64%. Found: I, 2.35; II, 2.40,

and no benzene could be detected in the vapors given off. This molecule of water is not lost when the product is placed in an evacuated desiccator over phosphorus pentoxide for several days, and is probably not water of crystallization (page 2500). The product from acetone, however, lost only about one-third of a molecule of water, showing that it was undoubtedly a mixture of the anhydrous material, and the hydrate. After water was driven off both products melted at 213° and analyses showed them to be the pure anhydrous dibenzoate.

The dibenzoate of phenoltetrachlorophthalein is readily soluble in acetone, benzene, and ethyl acetate; nearly insoluble in ethyl alcohol, methyl alcohol and ether. It is insoluble in 10% alkali in the cold. On warming, partial saponification slowly takes place.

As the entire amount of the anhydrous dibenzoate had a constant melting point of 213°, and in the course of fractional crystallization no indication of an isomer presented itself, it is highly probable that phenoltetrachlorophthalein is not a mixture of two isomers and is correctly represented by Formula I (page 2487).

As Orndorff and Hitch[1] had found that tetrachlorofluorescein gave only a monobenzoate by the Baumann-Schotten reaction, an attempt was made

---

[1] *J. Am. Chem. Soc.*, **36**, 692 (1914).

to obtain the monobenzoate of phenoltetrachlorophthalein, by this method using 10 g. of phenoltetrachlorophthalein, 9 g. potassium hydroxide and 10 g. of benzoyl chloride. The product after purification was found to melt at 213° and an analysis showed conclusively that it was the dibenzoate.

Subst., 0.2456, cc. 0.1 N $AgNO_3$, 14.75.
Calc. for $C_{34}H_{18}O_6Cl_4$: Cl, 21.36. Found: 21.30.

Dinitrophenoltetrachlorophthalein was made as follows: Ninety-six grams of phenoltetrachlorophthalein were heated with a mixture of 1500 g. of glacial acetic acid and 147 g. of sulfuric acid (sp. gr. 1.84) about one hour at 80°. The mixture was then cooled to 20°, and 49 g. of nitric acid (sp. gr. 1.42) gradually added. The temperature was raised to 50° by immersing the flask in hot water, complete solution of the phthalein resulting. Extreme care had to be taken at this point not to allow the temperature to rise above 50°, otherwise higher nitration products were formed in sufficient quantity to make the purification of the dinitro compound extremely difficult. The solution was then cooled to room temperature and stirred for 24 hours until no unchanged phenoltetrachlorophthalein could be detected. The nitration product, which crystallized out, was filtered off and washed several times with small amounts of alcohol to remove impurities which imparted to the alcohol an orange color. The yellow dinitro product was then fractionally crystallized from acetone. All fractions finally showed a constant melting point of 240°. A small portion crystallized from glacial acetic acid also melted sharply at 240°. By adding water to the original nitrating solution, a small amount of dinitro product separated as a light yellow flocculent precipitate. This was purified as described above. The yield of the purified product was about 80%. Fractions crystallized from both acetone and glacial acetic acid lost no weight on heating. The material dried at 130°, gave the following results on analysis:[1]

Subst., I, 0.2672; II, 0.2135; cc. 0.1 N $AgNO_3$; I, 19.57; II, 15.70.
Calc. for $C_{20}H_8Cl_4O_8N_2$: Cl, 25.98%. Found: I, 25.97; II, 26.08.
Subst., I, 0.3494; II, 0.3587; cc. 0.1 N HCl; I, 13.00; II, 13.25.
Calc. for $C_{20}H_8Cl_4O_8N_2$: N, 5.13%. Found: I, 5.21; II, 5.15.

Dinitrophenoltetrachlorophthalein is light yellow in color and dissolves in caustic alkalies and alkali carbonates, with a light yellow color, more concentrated solutions having an orange color. It is insoluble in alkali bicarbonates. It is somewhat soluble in glacial acetic acid and ethyl acetate, more readily soluble in acetone. It is comparatively insoluble in ether, ethyl alcohol, methyl alcohol, and benzene.

An attempt was made to obtain a hydrate, or a carbinol acid of the dini-

---

[1] In this work, all determinations of nitrogen were made by first reducing the nitro compounds by means of zinc dust and concentrated sulfuric acid, and then proceeding as in the Kjeldahl-Gunning method.

tro product by dissolving it in potassium hydroxide solution and precipitating with hydrochloric acid. On heating, the product lost no weight even at 200° and an analysis showed that it was the anhydrous dinitrophenoltetrachlorophthalein.

Subst., 0.2357; cc. 0.1 *N* $AgNO_3$, 17.19.
Calc. for $C_{20}H_8Cl_4O_8N_2$: Cl, 25.98. Found: 25.86.

All attempts to prepare dinitrophenoltetrachlorophthalein by the condensation of orthonitrophenol and tetrachlorophthalic anhydride, using such condensing agents as sulfuric acid (sp. gr. 1.84), fuming sulfuric acid (containing 15% of free sulfur trioxide) and freshly fused zinc chloride, were without success.

Action of Dry Ammonia on Dinitrophenoltetrachlorophthalein.—When treated with dry ammonia, the dinitro product gradually changed from light yellow to dark brown. Three molecules of ammonia were absorbed in a few hours. It, however, continued to gain weight slowly for four days when it absorbed four molecules of ammonia. When the salt was exposed to the air, the ammonia was gradually given off and the product returned to approximately the original weight. The small amount of ammonia which remained was readily driven off by heating at 80°.

Subst., I, 0.5182; II, 0.7526; gain in wt., I, 0.0625; II, 0.0942.
Calc. for $C_{20}H_8Cl_4O_8N_2.4NH_3$: NH_3, 11.10%. Found: I, 10.76; II, 11.12.

Dinitrophenoltetrachlorophthalein Dibenzoate.—Five grams of dinitrophenoltetrachlorophthalein were boiled with 35 g. of benzoyl chloride for a half hour. The dark brown solution was poured into ethyl alcohol when the benzoate separated as a dark brown oil. After considerable shaking, the oil solidified. It was recrystallized from benzene by the addition of ethyl alcohol, and obtained colorless with a sharp melting point of 205°. A fraction crystallized from acetone showed no change in melting point. This product was the hydrate (page 2500). Loss in weight determinations at 120° were made with fractions crystallized from a mixture of benzene and ethyl alcohol and also from acetone. In each case the vapors from the drying tube were conducted into a wash bottle containing water, but neither acetone nor ethyl alcohol could be detected in the water.

Subst., I, 0.9985; II, 0.4729; loss (water) at 120°, I, 0.0240; II, 0.0113.
Calc. for $C_{34}H_{16}Cl_4O_{10}N_2$: H_2O, 2.33%. Found: I, 2.40; II, 2.39.

The molecule of water is not lost on standing for days in an evacuated desiccator over phosphorus pentoxide. The product is, therefore, a hydrate. The anhydrous dibenzoate also melted sharply at 205° and gave the following results on analysis:

Subst., I, 0.2326; II, 0.2286; cc. 0.1 *N* $AgNO_3$; I, 12.31; II, 12.03.
Calc. for $C_{34}H_{16}Cl_4O_{10}N_2$: Cl, 18.81. Found: I, 18.77; II, 18.66.

Dinitrophenoltetrachlorophthalein dibenzoate is readily soluble in benzene, acetone and ethyl acetate. It is comparatively insoluble in methyl alcohol, ethyl alcohol, and ether. In hot 10% sodium hydroxide solution, the product is slowly, but only partially, saponified, the solution becoming orange in color.

By benzoylating dinitrophenoltetrachlorophthalein according to the Baumann-Schotten reaction, the same dibenzoate was obtained. The material melted sharply at 205° and, after drying to constant weight at 120°, gave the following result on analysis:

Subst., 0.2646, cc. 0.1 *N* $AgNO_3$, 14.18.
Calc. for $C_{34}H_{16}Cl_4O_{10}N_2$: Cl, 18.81%. Found: 19.01.

Hence, dinitrophenoltetrachlorophthalein, like phenoltetrachlorophthalein, does not give a monobenzoate by the Baumann-Schotten reaction.

Dinitrophenoltetrachlorophthalein Diacetate.—Ten grams of dinitrophenoltetrachlorophthalein were boiled for half an hour with 70 g. of pure acetic anhydride. The acetate was then extracted a few times with small amounts of boiling alcohol, in which it is practically insoluble. After crystallizing from benzene, pale yellow crystals were obtained melting at 136°. The air-dried product lost no weight on standing for several days in an evacuated desiccator over phosphorus pentoxide. The following results were obtained on analysis:

Subst., I, 0.2684; II, 0.2519; cc. 0.1 *N* $AgNO_3$; I, 16.24; II, 15.25.
Calc. for $C_{24}H_{12}Cl_4O_{10}N_2$: Cl, 22.52%; for $C_{24}H_{12}Cl_4O_{10}N_2.2H_2O$: Cl, 21.30%. Found: I, 21.46; II, 21.47.

On heating some of the air-dried substance in the electric oven to constant weight at 105°, one molecule of water is lost.

Subst., I, 0.4131; II, 0.4188; loss (water); I, 0.0114; II, 0.0120.
Calc. for $C_{24}H_{12}Cl_4O_{10}N_2$: H_2O, 2.78%. Found: I, 2.76; II, 2.86.

When the temperature was raised to 140°, the product melted and after heating five hours another molecule of water was lost.

Subst., I, 0.4131; II, 0.4188; loss (water); I, 0.0230; II, 0.0234.
Calc. for $C_{24}H_{12}Cl_4O_{10}N_2$: $2H_2O$, 5.41%. Found: I, 5.56; II, 5.59.

In the above determinations no benzene could be detected in the vapors from the material. The anhydrous material thus obtained gave the following results on analysis:

Subst., I, 0.3707; II, 0.4206; cc. 0.1 *N* $AgNO_3$; I, 23.45; II, 26.58.
Calc. for $C_{24}H_{12}Cl_4O_{10}N_2$: Cl, 22.52%. Found: I, 22.43; II, 22.41.

Some of the air-dried material which dissolved readily in benzene giving a colorless solution, was then dissolved in acetone and the solution was bright yellow in color. A fraction crystallized from acetone remained constant in weight when kept for several days in a vacuum over phosphorus pentoxide. Moreover, on heating in the electric oven at 105° for two hours, there was no loss in weight. When, however, the temperature was raised to 140°, the product melted and after heating five hours it became constant in weight, one molecule of water being lost. Acetone could not be detected in the vapors given off from the material. The substance then gave, on analysis, results for the anhydrous diacetate. Dinitrophenoltetrachlorophthalein diacetate, therefore, crystallizes from benzene with two molecules of water, one molecule being held more firmly than the other. It crystallizes from acetone with only one molecule of water.

Dinitrophenoltetrachlorophthalein diacetate is readily soluble in benzene, acetone and ethyl acetate, but almost insoluble in methyl and ethyl alcohols. It does not dissolve in cold 10% sodium hydroxide solution, but on warming partial saponification takes place, the solution becoming deep orange in color.

Monobromodinitrophenoltetrachlorophthalein.—Ten grams of dinitrophenoltetrachlorophthalein were suspended in 200 cc. of glacial acetic acid, and 6 g. of bromine in 25 cc. of glacial acetic acid added dropwise. The dinitro product did not dissolve on boiling the solution. Six grams more of bromine were then added, and the solution heated till the dinitro product was completely dissolved. The clear solution was poured into a large excess of water and the yellow precipitate crystallized from a mixture of acetone and ethyl alcohol. After recrystallizing a few times all fractions showed a sharp melting point of 220–221°. A fraction crystallized from glacial acetic acid showed no variation in the melting point.

The chlorine and bromine determinations on this compound were made by the method already described.[1] After heating, the contents of the tube were dissolved in *dilute* nitric acid, care being taken to keep the solution cold and to avoid large excess of nitric acid. (When these precautions were not taken, a yellow filtrate was always obtained on filtering off the carbon. This was due to free bromine which would be lost and cause low results in the halogen content.)

The following results were obtained on the material dried at 120°:

	Substance. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate.	Chlorine. Per cent.	Bromine. Per cent.
I	0.2243	0.2740	18.00 cc.	22.77	12.81
II	0.2441	0.2969	19.56 cc.	23.01	12.17
Calculated for $C_{20}H_7BrCl_4N_2O_8$				22.70	12.79

Subst., I, 0.3414; II, 0.3778; cc. 0.1 *N* HCl; I, 11.00; II, 11.89.

Calc. for $C_{20}H_7BrCl_4N_2O_8$: N, 4.48%. Found: I, 4.51; II, 4.41.

The monobromodinitrophenoltetrachlorophthalein was obtained as a bright yellow, crystalline compound, showing slightly more color than the dinitrophenoltetrachlorophthalein, and differing from the latter in its greater solubility in the ordinary solvents. The compound is readily soluble in caustic alkalies and alkali carbonates with a deep orange color. It is insoluble in alkali bicarbonates.

---

[1] *Am. Chem. J.*, **41**, 380 (1909).

Action of Dry Ammonia on Monobromodinitrophenoltetrachlorophthalein.—When placed in dry ammonia gas, this compound gradually absorbed five molecules of ammonia and came to constant weight in two days, changing in color from a bright yellow to a dark brown.

Subst., 0.5652; gain in wt., 0.0741.
Calc. for $C_{20}H_7BrCl_4N_2O_8.5NH_3$: NH_3, 11.99. Found: 11.59.

When this salt was placed in a tube and a current of dry air passed over it, three molecules of ammonia were lost within an hour. The diammonium salt is not stable and gradually loses ammonia on standing in a desiccator over calcium chloride, at the end of seven days less than one molecule of ammonia remaining. A small amount of ammonia is held indefinitely at room temperature. When, however, this product is heated to 100° for an hour, all ammonia is driven off, and the compound returns to its original color and weight.

Dibromodinitrophenoltetrachlorophthalein was obtained as follows: Ten grams of dinitrophenoltetrachlorophthalein were suspended in 200 cc. of glacial acetic acid, and 15 g. of bromine in 25 cc. of glacial acetic acid added. The solution was heated to boiling when the dinitro compound dissolved completely, and at the end of two hours a bright yellow precipitate began to separate from the boiling solution. It was then filtered and the product crystallized from acetone. After recrystallizing a few times, a small amount of a compound with a lower melting point, undoubtedly the monobromo compound, was separated. All fractions then melted sharply at 271–272°, with decomposition. A fraction from glacial acetic acid also had the same melting point. The following results were obtained on analysis:

Subst. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate.	Chlorine. Per cent.	Bromine. Per cent.
0.2787	0.3684	23.31 cc.	19.85	22.11

In the above determination the mixture of silver halides was treated with chlorine and the following results obtained:[1]

Subst. Gram.	Silver halides. Gram.	Decrease. Gram.	Chlorine. Per cent.	Bromine. Per cent.
0.2787	0.3684	0.0340	19.95	21.93
Calculated for $C_{20}H_6Br_2Cl_4N_2O_8$			20.15	22.71

Analysis of the compound for nitrogen gave the following results:

Subst., I, 0.4161; II, 0.3800; cc. 0.1 *N* HCl; I, 11.62; II, 10.33.
Calc. for $C_{20}H_6Br_2Cl_4N_2O_8$: N, 3.98. Found: I, 3.91; II, 3.81.

The dibromo compound differs from the monobromo product in its greater insolubility in acetone, glacial acetic acid, benzene, ethyl and methyl alcohols. It is soluble in acetone; less soluble in glacial acetic acid, and only sparingly soluble in methyl and ethyl alcohols and in

---

[1] *J. Am. Chem. Soc.*, **36**, 702 (1914).

benzene. It dissolves in caustic alkalies and alkali carbonates, with a reddish orange color. It is insoluble in alkali bicarbonates.

Action of Dry Ammonia on Dibromodinitrophenoltetrachlorophthalein.—This product absorbed five molecules of ammonia in 20 hours and changed from a bright yellow to a bright orange color.

Subst., I, 0.5286; II, 5294; gain in wt.; I, 0.0611; II, 0.0618.
Calc. for $C_{20}H_6Br_2Cl_4N_2O_8.5NH_3$: NH_3, 10.97%. Found: I, 10.36; II, 10.45.

When dry air was passed over this salt at room temperature, three molecules of ammonia were lost very readily, the product changing in color from a bright orange to a dark orange color. An analysis made by heating the salt to 125° and collecting the ammonia in standard tenth-normal hydrochloric acid solution, showed that the product was the diammonium salt.

Subst., 0.5530; cc. 0.1 *N* HCl, 13.85.
Calc. for $C_{20}H_6Br_2Cl_4N_2O_8.2NH_3$: NH_3, 4.61%. Found: 4.20.

When all of the ammonia was driven off, the product returned to the original weight and color of the dibromo compound. The diammonium salt is not stable in the air, but slowly loses ammonia and takes up moisture. In a desiccator over fused calcium chloride, the ammonia is slowly lost, less than one molecule remaining after standing ten days.

Diaminophenoltetrachlorophthalein.—Ten grams of dinitrophenoltetrachlorophthalein were heated with a solution of 100 cc. of absolute alcohol saturated with dry hydrochloric acid gas and 50 g. of crystallized stannous chloride on the water bath for a half hour. Complete reduction of the dinitro compound took place and a copious white precipitate of the double tin salt of the diamino compound separated. This was filtered off, washed with concentrated hydrochloric acid and dissolved in hot water. The tin was removed by passing hydrogen sulfide into the acidified solution and the colorless filtrate carefully neutralized with ammonia. The free base separated as a coffee-brown crystalline powder. It was recrystallized from ethyl alcohol by the addition of water and after crystallizing a few times, obtained as bright orange-colored crystals. The following results were obtained on analysis:

Subst., I, 0.2240; II, 0.2873; cc. 0.1 *N* $AgNO_3$; I, 18.50; II, 23.68.
Subst., 0.4979; cc. 0.1 *N* HCl, 19.87.
Calc. for $C_{20}H_{12}Cl_4N_2O_4$: N, 5.77%; Cl, 29.19%. Found: N, 5.59; Cl, I, 29.28; II, 29.23.

The diaminophenoltetrachlorophthalein does not melt even when heated to 335°. It turns dark, however, showing decomposition. It dissolves in caustic alkalies, alkali carbonates, and in ammonia, with a prussian blue color. These alkaline solutions, however, are unstable, and on long standing the color gradually disappears. The diamino compound does not dissolve in alkali bicarbonates. It dissolves in concentrated sulfuric acid with a pink color. On warming slightly no change takes place, but on adding a small amount of water, the solution becomes colorless. In concentrated hydrochloric acid, the bright orange crystals of the diamino compound are changed to those of the colorless hydrochloride.

Diaminophenoltetrachlorophthalein Dihydrochloride.—Two grams of the pure diamino compound were boiled for an hour with 200 cc. of hydrochloric acid solution (1 : 1). The colorless hydrochloride was then filtered off, washed with water containing hydrochloric acid, and dried in the air for one week. The following result was obtained on analysis of the air-dried product:

Subst., 0.1452; cc. 0.1 *N* $AgNO_3$, 15.50.
Calc. for $C_{20}H_{12}Cl_4N_2O_4.2HCl$: Cl, 38.07%. Found: 37.86.

The hydrochloric acid was determined by weighing portions of the air-dried material into Erlenmeyer flasks, adding water, and heating until the hydrochloride was decomposed. The insoluble free base was filtered off, and the acid in the filtrate determined by titration with standard alkali, enough of the diaminophenoltetrachlorophthalein remaining in solution to act as indicator.

Subst., I, 0.4956; II, 0.3089; cc. 0.1 *N* HCl, I, 17.40; II, 10.94.
Calc. for $C_{20}H_{12}Cl_4N_2O_4.2HCl$: HCl, 13.05%. Found: I, 12.80; II, 12.92.

The diaminophenoltetrachlorophthalein dihydrochloride is soluble in water but insoluble in water containing hydrochloric acid. When its aqueous solution is boiled, the salt is decomposed and the free diaminophenoltetrachlorophthalein crystallizes from the solution.

Tetranitrophenoltetrachlorophthalein.—This compound was made as follows: 60 g. of phenoltetrachlorophthalein were heated on the water bath to a temperature of 80–90° about an hour with 720 g. of sulfuric acid (sp. gr. 1.84). Complete solution took place and when a small portion was withdrawn and poured into water there was no precipitation of the phthalein, showing that complete conversion into the sulfonic acid had taken place. The solution was cooled to 0° and a mixture of 70 g. of nitric acid (sp. gr. 1.42) and 70 g. of sulfuric acid (sp. gr. 1.84) slowly added and the solution mechanically stirred for an hour, the temperature being allowed to rise to 35°. At the end of this time, the solution became cloudy and the yellow nitration product began to separate out. The nitration mixture was allowed to stand overnight and added to a large amount of water. The crude product was light yellow in color and the yield was about 80%. It was crystallized several times from acetone and obtained in the form of very fine needles, melting at 289–290°. Fractions crystallized from both nitrobenzene and glacial acetic acid showed no change in the melting point. Some of the product, crystallized from acetone, was dried in the air and a weighed amount placed in an evacuated desiccator over phosphorus pentoxide. It stood several days, and a small amount of mechanically-held solvent was lost. When this material was heated in a drying tube at 185°, two molecules of water were given off.

Subst., I, 0.4180; II, 0.6417; loss (water); I, 0.0211; II, 0.0344.
Calc. for $C_{20}H_6Cl_4O_{12}N_4.2H_2O$: H_2O, 5.36%. Found: I, 5.05; II, 5.36.

In order to prove that no acetone was given off, the vapors from the drying tube were passed into an absorption bottle containing water. No acetone could be detected by the iodoform reaction.

The anhydrous material gave the following results on analysis:

Subst., I, 0.2464; II, 0.2600; cc. 0.1 *N* $AgNO_3$; I, 15.57; II, 16.34.
Subst., 0.3333; cc. 0.1 *N* HCl, 21.27.
Calc. for $C_{20}H_6Cl_4O_{12}N_4$: N, 8.81%; Cl, 22.51%. Found: N, 8.94; and Cl, I, 22.41; II, 22.28.

The tetranitrophenoltetrachlorophthalein differs from the dinitrophenoltetrachlorophthalein in its greater insolubility in the ordinary organic solvents. It is comparatively soluble in acetone; soluble in acetic acid to the extent of less than one-half per cent., and practically insoluble in methyl and ethyl alcohols and in benzene. It dissolves in caustic alkalies and alkali carbonates with a clear yellow color, more concentrated solutions having an orange color. Unlike the dinitrophenoltetrachlorophthalein, it dissolves in alkali bicarbonates with a yellow color. This behavior shows the stronger acid properties of the tetranitro compound.

Action of Dry Ammonia on Tetranitrophenoltetrachlorophthalein.—The anhydrous compound was treated with dry ammonia gas. More than two molecules of ammonia were absorbed in less than one minute, and the product changed from yellow to a deep orange color. At the end of an hour four molecules of ammonia were absorbed, but the product continued to absorb ammonia very slowly for two days, increased very markedly in volume, and finally absorbed five molecules of ammonia.

Subst., I, 0.3975; II, 0.4540; gain in wt.; I, 0.0518; II, 0.0594.
Calc. for $C_{20}H_6Cl_4O_{12}N_4.5NH_3$: NH_3, 11.81%. Found: I, 11.53; II, 11.57.

The salt was placed in a tube and a current of *dry* air passed over it, previous work having shown that the salt was quite hygroscopic, absorbing moisture from the air and at the same time losing ammonia. In the course of a few hours, almost three of the five molecules of ammonia were lost. It was then placed in a vacuum over phosphorus pentoxide for several days. No weight was lost after the first day. This compound, according to the calculations from the amount of ammonia still held, was the diammonium salt. This was further verified by heating it at 150° and collecting the ammonia in an absorption bottle, containing standard hydrochloric acid solution. The excess hydrochloric acid was then titrated with standard ammonium hydroxide, using methyl red as indicator.

Subst., 0.3975, wt. of salt, 0.4176; cc. 0.1 *N* HCl, 11.80.
Calc. for $C_{20}H_{16}Cl_4O_{12}N_4.2NH_3$: NH_3, 5.09%. Found: 4.81.

After heating, the product returned to the original weight and color of the tetranitro compound.

Tetranitrophenoltetrachlorophthalein Dibenzoate.—This compound was prepared in the same way as the corresponding dinitro product (page 2490). The yield of the dibenzoate was practically quantitative, and the product appeared as very fine, almost colorless crystals. It was recrystallized from nitrobenzene by the addition of ethyl alcohol. On heating the air-dried product to 135°, no loss in weight ensued. The following results were obtained on analysis:

Subst., I, 0.2269; II, 0.2805; cc. 0.1 *N* $AgNO_3$; I, 10.69; II, 13.21.
Calc. for $C_{34}H_{14}Cl_4O_{14}N_4$: Cl, 16.81%. Found: I, 16.71; II, 16.70.

The tetranitrophenoltetrachlorophthalein dibenzoate melts with decomposition at 285°. It dissolves readily in hot nitrobenzene, but is practically insoluble in methyl and ethyl alcohols, ethyl acetate, acetone, ether, benzene, and xylene. It is insoluble in cold dilute sodium hydroxide. On boiling, partial saponification takes place, the supernatant liquid becoming orange in color.

An attempt was made to prepare a benzoate of tetranitrophenoltetrachlorophthalein by means of the Baumann-Schotten reaction. Instead of the expected benzoyl derivative, a potassium salt of tetranitrophenoltetrachlorophthalein was obtained.

Tetranitrophenoltetrachlorophthalein Diacetate.—This compound was prepared in the same way as the corresponding dinitro product (page 2491). It was crystallized from ethyl acetate and obtained in pale yellow crystals, which did not possess a sharp melting point, becoming molten when heated in a melting point tube to 200°. The following results were obtained on analysis:

Subst., I, 0.2568; II, 0.2392; cc. 0.1 *N* $AgNO_3$; I, 14.20; II, 13.20.
Calc. for $C_{24}H_{10}Cl_4O_{14}N_4$: Cl, 19.70%. Found: I, 19.61; II, 19.57.

Tetranitrophenoltetrachlorophthalein diacetate is readily soluble in xylene and ethyl acetate. It is practically insoluble in methyl and ethyl alcohols, ether, acetone, and benzene. When boiled with dilute caustic alkali, it saponifies slowly, but only partially.

Tetraaminophenoltetrachlorophthalein.—Eight grams of tetranitrophenoltetrachlorophthalein were heated on a boiling water bath with 150 cc. of alcohol saturated with dry hydrochloric acid gas, and containing 80 g. of crystallized stannous chloride. The solution was diluted with a large amount of water and evaporated to about one-third of the original volume, in order to get rid of the alcohol. No separation of the amino compound or the tin chloride double salt took place, even on long standing. Hydrogen sulfide was then passed through the solution, diluted to 250 cc., until all the tin was removed. The filtered solution was evaporated to small bulk and carefully *neutralized* with ammonium hydroxide. The free base appeared as chocolate brown flocks, which were filtered off and dried. By crystallizing from ethyl alcohol, the tetraamino compound was obtained as a light brown, crystalline powder, which did not melt even when heated to 335°. The yield was very small, less than one gram of the purified product being obtained. The following results were obtained on analysis:

Subst., 0.2660; cc. 0.1 N $AgNO_3$, 20.48.
Calc. for $C_{24}H_{14}Cl_4O_4N_4$: Cl, 27.49%. Found: 27.30.

Tetraaminophenoltetrachlorophthalein differs markedly from the corresponding diamino compound in its greater solubility in the ordinary solvents. It dissolves readily in water while the diamino compound is almost insoluble. It dissolves in caustic alkalies and alkali carbonates with a blue color, which is not nearly as intense as that produced by the diamino compound. The alkaline solutions when exposed to the air are much more unstable than those of the diamino compound, the blue color soon changing to green and finally to a straw color.

Theoretical.

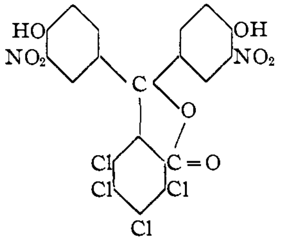
By the action of nitric acid on phenoltetrachlorophthalein, a dinitro- and a tetranitro-derivative have been prepared. Although the positions of the nitro groups in these compounds have not been proven in this paper, it is logical to assume that the nitro groups enter each phenol molecule in the ortho positions to the hydroxyl groups and in the meta positions to the tetrachlorophthalic acid residue. Schestakoff and Nocken[1] state that both nitro groups in *dinitrophenolphthalein* are in the same phenol residue, but the evidence which they present to establish this view is by no means conclusive.[2] Although these nitro compounds of phenoltetrachlorophthalein are light yellow in color, it is probable that the color is due to the chromophoric action of the nitro groups and therefore the lactoid formula should be assigned to them. The ortho position of the nitro group in the phenol molecule probably conditions the color to some extent; for instance, orthonitrophenol has a marked yellow color, while paranitrophenol is colorless. From the above considerations the following formulas are assigned to the nitrophenoltetrachlorophthaleins (page 2499).

Dinitrophenoltetrachlorophthalein crystallizes from solvents in the anhydrous condition, while the tetranitro compound holds two molecules of water, which are not lost on remaining several days in a vacuum over phosphorus pentoxide. Since the latter compound dissolves readily in alkali bicarbonates, it can best be represented as a hydrate of the carbinol carboxylic acid.

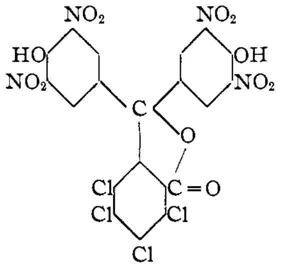
---

[1] *Ber.*, 47, 331 (1914).

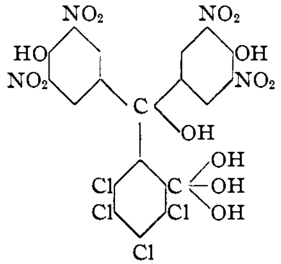
[2] Oddo, *Gazz. chim. ital.*, 43, II, 175 (1913) and *Ber.*, 47, 967 (1914).



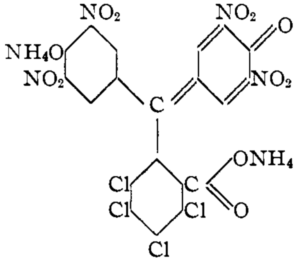
Dinitrophenoltetrachlorophthalein.



Tetranitrophenoltetrachlorophthalein.

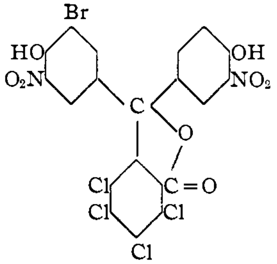


The fact that the tetranitro compound holds two molecules of water, while the dinitro derivative crystallizes in the anhydrous form, may be explained by the more marked acid properties of the former. This is clearly shown by the fact that tetranitrophenoltetrachlorophthalein dissolves in alkali bicarbonates while the dinitro derivative does not, and also by the fact that tetranitrophenoltetrachlorophthalein absorbs *five* molecules of ammonia while the dinitro compound absorbs but *four*. When these abnormal salts are exposed to the air the dinitro compound loses practically all of its ammonia while the tetranitro derivative forms a stable diammonium salt. This latter compound has a deep orange color and is best represented by the following quinoid formula:

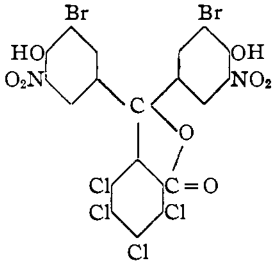


Diammonium salt of tetranitrophenoltetrachlorophthalein.

Monobromo- and dibromodinitrophenoltetrachlorophthaleins have been made by the bromination of dinitrophenoltetrachlorophthalein. These compounds have acid properties intermediate between those of the dinitro- and tetranitrophenoltetrachlorophthaleins. That both of these bromo compounds have stronger acid properties than dinitrophenoltetrachlorophthalein is shown by the fact that they absorb more ammonia and that they have weaker acid properties than the tetranitrophenoltetrachlorophthalein by the fact that they do not decompose alkali bicarbonates. These compounds are therefore best represented by lactoid formulas.

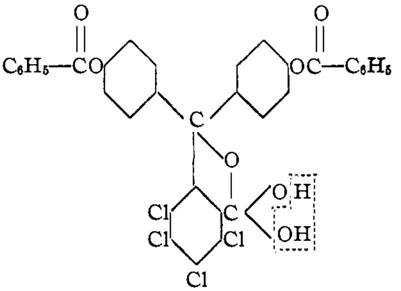


Monobromodinitrophenoltetrachlorophthalein.

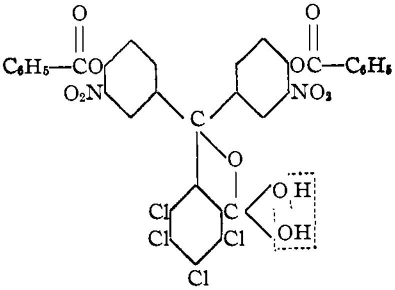


Dibromodinitrophenoltetrachlorophthalein.

Phenoltetrachlorophthalein and dinitrophenoltetrachlorophthalein form colorless dibenzoates. Both crystallize from benzene with a molecule of water which is not lost on remaining several days in a vacuum over phosphorus pentoxide. In each case this form is probably the hydrate and not the carbinol acid since they are both insoluble in cold caustic alkalies.



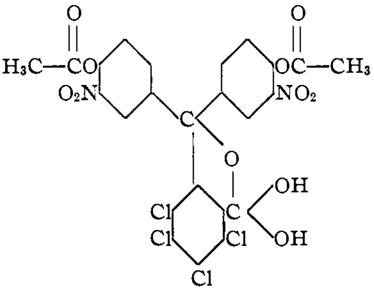
Hydrate of phenoltetrachlorophthalein dibenzoate.



Hydrate of dinitrophenoltetrachlorophthalein dibenzoate.

On heating to 120°, both compounds lose the molecule of water, as shown in the above formulas.

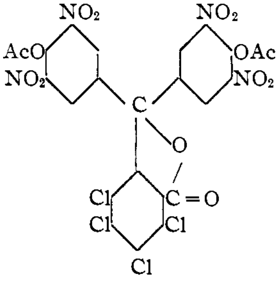
Dinitrophenoltetrachlorophthalein diacetate crystallizes from benzene in very pale yellow crystals, which hold two molecules of water, neither of which is lost on remaining several days in a vacuum over phosphorus pentoxide. On heating to 105° for an hour, one molecule of water is lost, and after continued heating at 105°, or more readily at 140°, the compound melts and the second molecule of water is lost. From acetone the compound crystallizes with only one molecule of water, which is lost only at 140°. It seems highly probable, therefore, that the product from acetone is the hydrate



while the product from benzene is this hydrate with a molecule of water of crystallization. The fact that the substance is not soluble in the cold in caustic alkalies shows that it is not the carbinol carboxylic acid.

Oddo[1] made dinitrophenolphthalein diacetate, which he describes as a dimorphous body. It is very probable that the white product obtained by him from benzene is a hydrate, while the yellow form, obtained either by heating the white modification above its melting point, or by crystallizing it from alcohol, is the anhydrous diacetate.

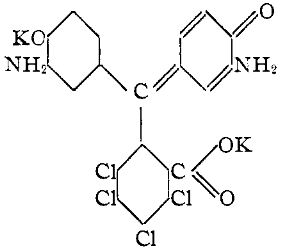
Tetranitrophenoltetrachlorophthalein forms a colorless dibenzoate, and a very pale yellow diacetate. Since these compounds are insoluble in alkalies and possess little color, they probably have the lactoid structure and may be represented by the following formula in which Ac represents an acetyl or a benzoyl group:



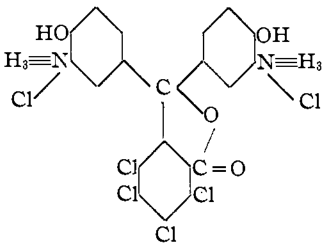
Diaminophenoltetrachlorophthalein is obtained by the reduction of dinitrophenoltetrachlorophthalein. It dissolves in alkalies with an intense Prussian blue color, while with hydrochloric acid it forms a colorless dihydrochloride, thus exhibiting the properties of both an acid and a base. That the basic properties are weak is shown by the fact that the hydrochloride is readily hydrolyzed by heating its aqueous solution. The structure of these compounds is best represented by the following formulas:

---

[1] *Gazz. chim. ital.*, 43, II, 175 (1913).

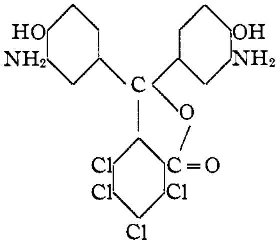


Dipotassium salt of diaminophenoltetrachlorophthalein (colored).

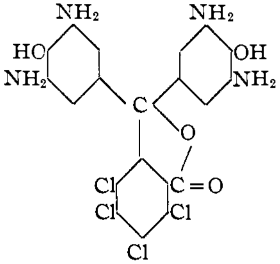


Dihydrochloride of diaminophenoltetrachlorophthalein (colorless).

Tetraaminophenoltetrachlorophthalein results from the reduction of tetranitrophenoltetrachlorophthalein. Unlike the diaminophenoltetrachlorophthalein, it is readily soluble in hydrochloric acid solution. It dissolves in alkalies with only a faint blue color, which soon disappears on standing, probably owing to the formation of the salt of the carbinol acid. Diamino- and tetraaminophenoltetrachlorophthalein probably are best represented by the following structural formulas:



Diaminophenol-tetrachlorophthalein.



Tetraaminophenol-tetrachlorophthalein.

It is interesting to note that these phthaleins are *colored* (possibly due to an orthoquinoid condition) and that they form *colorless* salts with acids.

Summary.

The results of this investigation may be briefly stated as follows:

1. Phenoltetrachlorophthalein has been made from tetrachlorophthalic acid and shown to be a chemical individual and not a mixture of isomers. In all probability both hydroxyl groups occupy the para positions to the methane carbon atom.

2. Dinitro- and tetranitrophenoltetrachlorophthalein have been prepared and the action of ammonia on these compounds has been studied.

3. The diacetates and the dibenzoates of the nitro compounds have been made, thus showing the presence of two hydroxyl groups.

4. The corresponding amino compounds have been obtained by the reduction of the nitro compounds. These compounds have both acid and

basic properties, dissolving in alkalies with a *blue* color and forming *colorless* hydrochlorides.

5. Monobromo- and dibromodinitrophenoltetrachlorophthalein have been prepared and the action of ammonia on these compounds has been studied.

6. The effect of introducing acid groups into the phenoltetrachlorophthalein molecule has been studied. Tetranitrophenoltetrachlorophthalein has the strongest acid properties; dinitrophenoltetrachlorophthalein the weakest, while the monobromo- and dibromodinitrophenoltetrachlorophthalein stand intermediate.

ITHACA, N. Y.

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

THE PYROGENETIC DECOMPOSITION OF AMIDES. I.

BY R. S. BOEHNER AND C. E. ANDREWS.

Received September 11, 1916.

It is a well-known fact that, on distillation, the acid amides of both the aliphatic and aromatic series decompose to a very slight degree into the corresponding cyanides and water. Wöhler and Liebig[1] passed the vapor of benzamide through a red hot glass tube obtaining a small quantity of an oily liquid which was later identified as phenyl cyanide. In view of the decomposition of alcohols into ethylene hydrocarbons, or ethers, and water, on being passed through hot tubes filled with various materials,[2] it was thought possible that a more complete decomposition of the amides into cyanides and water might be effected by a similar method. Since the products of decomposition of amides, namely the cyanides and water, have a much lower boiling point than the amides, it was thought that the method referred to above might be modified by heating the amides with the contact material in a flask whose outlet was high enough to permit the cyanides and water to distill off, but would cause the amides to condense in the flask and drop back upon the hot contact material. The contact substances used were aluminium oxide, pumice stone, glass, sand, and graphite. By the above method and using the substances mentioned a much more complete decomposition of the amides into the cyanides and water was effected.

Experimental.

A round-bottomed flask of 100 cc. capacity, containing the contact substance and amide, and provided with a ground-glass stopper with the outlet tube about 25 cm. above the bottom of the glass, was heated in an asbestos air bath. The heating was in each case regulated so that the

---

[1] *Ann.*, **3**, 249 (1832).

[2] Ipatiew, *Ber.*, **34**, 596, 3579 (1901); *Ibid.*, **35**, 1047, 1057 (1902); *Ibid.*, **36**, 1990 (1903); Sabatier and Mailhe, *Compt. rend.*, **146**, 1376 (1908); *Ibid.*, **147**, 106 (1908); *Ibid.*, **148**, 1734 (1909).