Subst. 0.1722, 0.0950; cc. of 0.1 *N* $Na_2S_2O_3$, 7.80, 4.62. Calc. for $(C_{19}H_{13}ClBr)$-NHCl: active Cl, 8.71%. Found: 8.03, 8.62.

Rearrangement of *p*-Bromophenyl-*p*-chlorophenyl-phenylmethylchloroamine.—This substance was heated with soda-lime in a metal bath at 200 to 210° for five minutes in order to effect its rearrangement. The extraction with benzene was carried out as explained before and the hydrolysis of the resulting mixture of arylimidobenzophenones yielded a mixture of ketones (*p*-chlorobenzophenone, *p*-bromobenzophenone, and *p*-bromo-*p*-chlorobenzophenone) and an aqueous solution of the hydrochlorides of *p*-chloroaniline, *p*-bromoaniline, and aniline. This mixture of the aniline hydrochlorides was made alkaline and extracted with ether, and the hydrochlorides reprecipitated with a freshly made solution of hydrogen chloride in absolute ether. The resulting crystalline mass was further purified by precipitation by ether from absolute alcohol solution and the product and then carefully dried *in vacuo*.

The proportions of aniline, *p*-chloroaniline, and *p*-bromoaniline in the hydrolyzed product of the above rearrangement were found by determinations of the hydrochloric content of, and the bromine absorbed by, a definite weight of the mixed hydrochlorides.

We have then the three simultaneous equations, $0.1295x + 0.164y + 0.2084z = a$; $60x + 40y + 40z = b$; and $x + y + z = c$. In these equations, x, y and z represent, respectively, the millimols of aniline hydrochloride, chloroaniline hydrochloride and bromoaniline hydrochloride present in a given weight a of the mixed salts, b is the number of cc. of 0.1 *N* $KBrO_3$ used to brominate the salts, and c represents the number of cc. of *N* NaOH (1/100 of the volume of 0.01 *N* solution actually used) required to neutralize the same weight of the mixed hydrochlorides. In carrying out the determinations, the titration with alkali is made first, phenolphthalein being the indicator, and the same solution is used for the bromination process. In view of the determinations representing an indirect method for three unknown components, the molecular weights of two of which are not very far apart, the method gives only approximate results.

Subst. 0.0315, 0.0262 and 0.0573 g.; cc. of 0.1 *N* $KBrO_3$, 9.11, 7.47, 15.23; cc. of 0.01 *N* NaOH, 19.35, 15.94, 33.14.

	Molar percentages.			Average.
Aniline hydrochloride	35.3	34.4	29.8	33
Chloroaniline hydrochloride	40.0	38.10	27.0	35
Bromoaniline hydrochloride	24.7	27.5	43.2	32

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

DIETHYLAMINO-*m*-HYDROXYBENZOYLTETRACHLOROBENZOIC ACID AND TRICHLORODIETHYLAMINOXANTHONECARBOXYLIC ACID AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND C. C. ROSE.

Received August 3, 1916.

Historical.

Diethylamino-*m*-hydroxybenzoylbenzoic acid is first mentioned by Graebe, Kohn and Huguenin.[1] They obtained it by fusing tetraethylrhod-

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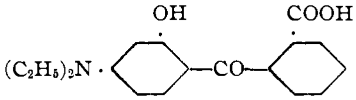
[1] *Archives des sciences physiques et naturelles de Genève*, **2**, 91 (1893).

amine with soda, the decomposition of the rhodamine being analogous to that of fluorescein into dioxybenzoylbenzoic acid[1] (page 2115).

In 1896, a German patent was granted the Basler Chemical Company covering a method of preparing new condensation products from phthalic acid anhydride and the dialkylmetamino-phenols.[2] This method, as applied to the diethyl acid, is as follows: 15 kg. of phthalic acid anhydride are dissolved in 75 kg. of toluene and 16.5 kg. of diethyl-*m*-aminophenol added. The solution is boiled for several hours, until there is no further increase in the crystalline precipitate, which separates after some time. The product is purified by crystallization from alcohol. It behaves like an amino acid, since it forms salts with both bases and mineral acids. The melting point cannot be sharply determined. Above 180°, it decomposes forming a red liquid. From the method of formation and the properties of the compound, the following formula is given to it:



Later the Basler Chemical Company was granted another patent[3] covering a new method for the preparation of this compound as follows: 17 kg. of diethyl-*m*-aminophenol are melted at 100° and 15 kg. of phthalic acid anhydride added. The temperature is held at 100° until the mass completely solidifies. It is then extracted with a small quantity of alcohol and the residue purified by crystallization from alcohol.

Haller and Guyot[4] were the first to make a scientific investigation of this compound. They prepared it according to the patents of the Basler Chemical Company and describe it as being made up of small white needles which decompose at 203° and which are but slightly soluble in alcohol even on warming.

Haller and Umbgrove[5] describe later the preparation of *p*-diethylaminobenzoyltetrachloro-*o*-benzoic acid,

$$(COOH)C_6Cl_4COC_6H_4N(C_2H_5)_2.$$

With acetic anhydride, this acid gave a mixed anhydride, to which they assign the formula

$$(CO.O.COCH_3)C_6Cl_4CO.C_6H_4.N(C_2H_5)_2.$$

They state that the acid cannot be esterified by the ordinary method and they prepared the esters by heating the mixed anhydride with sodium alcoholate.

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[1] Baeyer, *Ann.*, **183**, 23 (1876).

[2] D. R. P. 85931, *Frdl.*, **4**, 260.

[3] D. R. P. 87068, *Ibid.*, **4**, 262.

[4] *Compt. rend.*, **126**, 1248 (1898).

[5] *Bull. soc. chim.*, **25**, 598 (1901).

Later the same authors[1] prepare diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid according to the German patent 87068. Diethyl-*m*-aminophenol is melted on the water bath and the calculated amount of tetrachlorophthalic acid anhydride added. At the end of three hours the reaction is complete. It is brought about more rapidly when the temperature of the mixture is raised to 150° and the mass is stirred. The product is extracted with a small quantity of alcohol to dissolve any tetrachlororhodamine formed, and the products not entering into the reaction. Crystallized from alcohol it melts at 198° to a red liquid. Analyses gave the following results:

Calc. for $C_{18}H_{15}Cl_4NO_4$: C, 47.89; H, 3.32; N, 3.10; Cl, 31.48. Found: C, 47.76; H, 3.53; N, 3.27; Cl, 31.30 (page 2106).

In 1901, a patent[2] was granted to the Farbwerke vormals Meister, Lucius und Brüning covering the preparation of phthalic acid dyes of the naphthalene series, in which is described the preparation of diethylaminohydroxybenzoyldichloro- and -tetrachlorobenzoic acids.

For the former, 108 parts of dichlorophthalic acid anhydride, 82.5 parts of diethyl-*m*-aminophenol and 650 parts of toluene are heated to boiling for about 10 hours. The product is freed from toluene, dissolved in soda solution (93 g. Na_2CO_3 to one liter H_2O) and the solution heated. On cooling, an oil separates consisting of the sodium salt of the new acid and the diethyl-*m*-aminophenol not entering into the reaction. It is purified by dissolving in water, precipitating with sodium carbonate, redissolving in water and extracting the diethyl-*m*-aminophenol with ether. The dichloro acid precipitated out of the solution of the sodium salt by acetic or hydrochloric acid is amorphous, insoluble in water, soluble in alcohol and chloroform, and, in the pure condition, in excess of sodium carbonate solution without the separation of the oily sodium salt.

The tetrachloro acid is prepared from tetrachlorophthalic acid anhydride and diethyl-*m*-aminophenol in the same way as the dichloro acid and is like the latter in nearly all respects, only it is far more difficultly soluble in chloroform. It forms a sodium salt that even in the pure condition separates as an oil on the addition of excess of sodium carbonate solution.

Bloch[3] in 1913 prepared *dimethyl*amino-*m*-hydroxybenzoyltetrachlorobenzoic acid by heating equal molecules of *dimethyl*metaminophenol and tetrachlorophthalic acid anhydride in xylene. The solvent was distilled off, the material dissolved in sodium carbonate solution, precipitated by a dilute acid and purified by crystallization from acetic acid or dilute alcohol.

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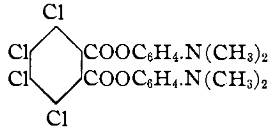
[1] *Bull. soc. chim.*, **25**, 747 (1901).

[2] D. R. P. 118077, *Frdl.*, **6**, 276.

[3] *Bull. de la Société Industrielle de Mulhouse*, **83**, 81 (1913).

He states that "besides the benzoylbenzoic acid, the presence of a yellow colored derivative was observed, insoluble in alkalies and which gave a colorless salt with hydrochloric acid. It crystallized from glacial acetic acid in yellow needles." He gives no analysis of this product, but thinks it may result from the esterification of dimethyl-*m*-aminophenol with tetrachlorophthalic acid anhydride (page 2113).



This investigation was undertaken for the purpose of determining the best conditions for preparing diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and to study its properties, chemical reactions and some of its derivatives. It seems probable that this acid is an intermediate product in the formation of tetrachlororhodamine and hence it was thought that its study would throw some light on this important class of dyes.

Experimental.

In the following pages all chlorine determinations were made by the lime method.[1] The nitrogen determinations were made by the Kjeldahl method, with the added precaution that the digestion was extended over a period of about three hours after the solution had become colorless. This was to insure complete transformation of all the nitrogen to ammonia, as nitrogen which splits off from a compound as an amine (diethylamine in this case) is difficultly transformed into ammonia in the Kjeldahl reaction. The drying tube used to bring the substances to constant weight was the electrically heated one described by Chamot and Pratt,[2] and more in detail by Orndorff and Nichols.[3] As most of the compounds described have decomposition points instead of melting points, and these show a tendency to vary with the speed of heating, it might be well to say here that the temperatures of decomposition were determined in an electrically heated Thiele apparatus which was so regulated as to give a rise in temperature of about 1° in 3 seconds. All temperatures of decomposition and melting points given, are uncorrected.

The diethyl-*m*-aminophenol used was very kindly furnished by the Badische Anilin- und Soda-Fabrik. It was in dark colored lumps but quite pure. Just before using it was always purified by distillation in a vacuum, as described by Meyenburg.[4] When exposed to the air, it quickly reddens. In order to determine its purity it was distilled under reduced pressure, the receiver being changed after the temperature had

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[1] *Am. Chem. J.*, **41**, 397 (1909).

[2] *J. Am. Chem. Soc.*, **32**, 635 (1910).

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

[4] *Ber.*, **29**, 502 (1896).

become constant, and a nitrogen determination was made on the second fraction.[1]

Subst., I, 0.3659; II, 0.6142; cc. 0.1 *N* HCl, I, 21.10; II, 37.89.
Calc. for $HO.C_6H_4.N(C_2H_5)_2$: N, 8.48%. Found: N, I, 8.08; II, 8.64.

The sulfuric acid became colorless after digesting for one hour. The first determination was stopped at this point while the second was run for three hours longer.

The tetrachlorophthalic acid anhydride was prepared by heating pure tetrachlorophthalic acid to 105°. The purity of the anhydride was checked by molecular weight determinations, made by titrating a weighed sample with standard alkali.[2]

Subst., I, 0.1304; II, 0.1774; cc. 0.1 *N* NaOH, I, 9.13; II, 12.42.
Calc. for $C_8Cl_4O_3$: M. W. 285.8. Found: I, 285.7; II, 285.8.

Hydroxyphenyldiethylammoniumdiethylaminometoxybenzoyltetrachlorobenzoate.—When diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride condense, under such conditions that tetrachlororhodamine formation does not take place, the product resulting is made up of two molecules of the diethyl-*m*-aminophenol to one of the tetrachlorophthalic acid anhydride and not one molecule to one molecule as Haller and Umbgrove state (page 2103). The condensation was brought about, both in toluene according to the German patent 118077 (page 2103), and by heating a mixture of the two components as described by Haller and Umbgrove (page 2103). The following are the detailed experiments:

(*a*) One molecule of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride in toluene solution.

Twelve grams of diethyl-*m*-aminophenol were dissolved in toluene and a solution of 20 g. of tetrachlorophthalic acid anhydride in toluene added. When the two nearly colorless solutions were mixed, a red color developed. The solution was heated to boiling and after several hours a white precipitate began to settle from the boiling toluene. When this precipitate no longer increased in amount (which required about 20 hours) the boiling was stopped. The product consisting of white needles was filtered off and washed with methyl alcohol. Yield 17.9 g. corresponding to 80% of the calculated amount (figured from the diethyl-*m*-aminophenol). The filtrate evaporated to dryness left a residue of between 5 and 6 g., which was found to be mostly tetrachlorophthalic acid anhydride.

(*b*) Two molecules of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride in toluene solution.

The procedure was exactly the same as in (*a*) except that 18 g. of diethyl-*m*-aminophenol and 18 g. of tetrachlorophthalic acid anhydride

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[1] International atomic weights (1916) are used in this paper.

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

were used. This allows for a slight excess of the anhydride. Yield 29.3 g. corresponding to 87% of the calculated amount.

(*c*) Fusion: one molecule of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride.

Twelve grams of diethyl-*m*-aminophenol and 20 g. of tetrachlorophthalic acid anhydride were fused in an atmosphere of carbon dioxide at 120° and at the same time the fused mass was stirred. After the melted mass became solid, it was crystallized once from toluene to remove any of the unchanged components. Yield 15 g. corresponding to 67% of the calculated amount.

(*d*) Fusion: two molecules of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride.

Thirty-six grams of diethyl-*m*-aminophenol and 36 g. of tetrachlorophthalic acid anhydride were fused as in (*c*). The melted mass thickened appreciably in ten minutes and was solid in half an hour. At first the temperature of the fused mass was about 30° to 45° higher than the temperature of the bath, but at the end of about 20 minutes it began to drop. During the fusion the contents of the flask *lost no weight.* The product, which had a bluish violet color, was crystallized once from toluene. Yield 65 g. corresponding to 96% of the calculated amount.

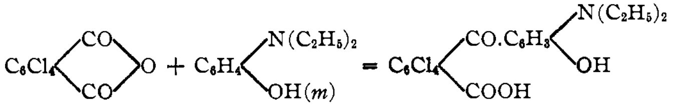
The condensation product crystallizes from methyl alcohol in prisms, containing no solvent of crystallization, which grind to a powder having a very faint yellowish tinge. It decomposes at 198° to a red liquid. When dried at 130° to constant weight, all products gave the same results on analysis.

Subst., *a*, 0.1610; *b*, 0.2873; *c*, 0.2280; *d*, 0.2768; cc. 0.1 *N* $AgNO_3$, *a*, 10.45; *b*, 18.64; *c*, 14.76; *d*, 17.95.

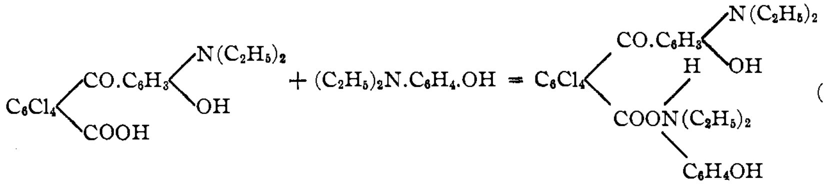
Subst., *b*, 0.7282; *d*, 0.3345; cc. 0.1 *N* HCl, *b*, 23.68; *d*, 10.51.

Calc. for $C_{23}H_{30}N_2O_5Cl_4$: Cl, 23.02; N, 4.55. Found: Cl, *a*, 23.02; *b*, 23.01; *c*, 22.96; *d*, 22.99; N, *b*, 4.56; *d*, 4.42.

It is therefore the result of the condensation of two molecules of diethyl-*m*-aminophenol with one molecule of tetrachlorophthalic acid anhydride as shown in the following equations:



(1)



(2)

Hydroxyphenyldiethylammoniumdiethylamino-*m*-hydroxybenzoyltetra-chlorobenzoate is slightly soluble in benzene, more so in toluene and xylene. It is soluble in methyl and ethyl alcohols, glacial acetic acid, and acetone; insoluble in water. It dissolves in solutions of caustic alkalies, alkali carbonates and ammonium hydroxide with a yellow color which gradually darkens. After some time a bright yellow precipitate forms which was found to be a salt of an acid containing but three atoms of chlorine. This trichloro acid will be taken up in detail later (page 2111). The removal of one atom of chlorine takes place very quickly when the alkaline solutions are heated to their boiling points which was proven in the following way: A weighed quantity of the tetrachloro product was dissolved in 2.5% aqueous potassium hydroxide and the solution heated until the potassium salt of the trichloro acid had entirely separated. The solution was made strongly acid, with concentrated nitric acid and filtered. An excess of standard silver nitrate solution was added to the filtrate and the silver chloride removed. The silver nitrate in the filtrate was titrated with standard ammonium thiocyanate. The weight of chlorine equivalent to the volume of standard silver nitrate solution used up, gave the weight of chlorine removed from the tetrachloro product.

Subst., I, 0.6250; II, 0.7867; cc. 0.1 *N* $AgNO_3$, I, 9.62; II, 12.18.

Calc. for one atom Cl, grams, I, 0.03594; II, 0.04524. Found: Cl, grams, I, 0.03414; II, 0.04318.

On account of the darkening of the alkaline solutions of the tetrachloro product, it was concluded that the second molecule of the diethyl-*m*-aminophenol is present in the form of a substituted ammonium radical and that the darkening is due to the fact that this second molecule is split off by the alkali and then the case is simply one of the increased sensitiveness of the alkylaminophenol in alkaline solution to the action of the oxygen of the air. If this is so, then concentrated mineral acids, as well as alkalies, should split off this second molecule of diethyl-*m*-aminophenol, and give the tetrachloro acid. This actually takes place under the influence of an alkali or a mineral acid.

(*a*) 24.8 g. of the original tetrachloro condensation product were dissolved in cold 5% aqueous sodium hydroxide and *immediately* poured into dilute sulfuric acid. A yellow product separated which weighed 17.8 g., corresponding to 99% of the calculated amount. It crystallized from methyl alcohol in the form of light yellow prisms, which decomposed at 217° forming a red liquid.

(*b*) Some of the original tetrachloro condensation product was dissolved in cold concentrated sulfuric acid, and the solution poured into distilled water kept cold by a freezing mixture. Reddish flakes separated. By crystallization from alcohol, a yellow product was finally obtained which decomposed at 217° forming a red liquid.

When dried to constant weight at 130°, analyses of both products proved them to be the tetrachloro acid.

Subst., I, 0.2156; II, 0.2500; cc. 0.1 *N* $AgNO_3$, I, 19.16; II, 22.27.

Subst., I, 0.4631; II, 0.5673; cc. 0.1 *N* HCl, I, 10.46; II, 13.17.

Calc. for $C_{18}H_{15}O_4NCl_4$: Cl, 31.45; N, 3.11. Found: Cl, I, 31.52; II, 31.59; N, I, 3.16; II, 3.25.

Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acid.—This acid crystallizes from methyl alcohol, ethyl alcohol, acetone and ether in pale yellow prisms containing no solvent of crystallization. It dissolves in solutions of the caustic alkalies, alkali carbonates and ammonium hydroxide with a yellow color *which does not darken on standing.* It is but slightly soluble in benzene and toluene; insoluble in water. That the tetrachloro acid loses an atom of chlorine when heated with caustic alkalies was proven in the same way as with the original condensation product (page 2107).

Subst., I, 0.6448; II, 0.7234; cc. 0.1 *N* $AgNO_3$, I, 13.91; II, 15.29.

Calc. for one atom Cl, grams, I, 0.05068; II, 0.05686. Found: Cl, grams, I, 0.04931; II, 0.05423.

In 10% solutions of the caustic alkalies there is no separation of the yellow colored salt of the trichloro acid until the solution is heated or diluted with water (page 2117).

Action of Dry Ammonia Gas on the Tetrachloro Acid.—A weighed quantity of the acid, dried at 130°, was treated with dry ammonia gas. It absorbed ammonia very rapidly at first, becoming slightly brighter yellow in color, and at the end of 24 hours had reached constant weight, showing an increase corresponding to two molecules of ammonia.

Subst., 0.6477; gain, NH_3, 0.0507.

Calc. for $C_{18}H_{13}O_4NCl_4(NH_4)_2$: NH_3, 7.02. Found: NH_3, 7.26.

When a current of dry air is passed over this diammonium salt it loses one molecule of its ammonia and becomes constant in weight. The monoammonium salt is hygroscopic.

Silver Salt of the Tetrachloro Acid.—Five grams of the tetrachloro acid were dissolved in absolute alcohol and 70 cc. of an alcoholic solution of silver nitrate (32 g. to the liter) added. After some time the silver salt precipitated in the form of yellow crystals. These were analyzed for silver as follows: A weighed amount was dissolved in concentrated nitric acid, poured into distilled water, the tetrachloro acid filtered off and the silver determined by titrating with standard ammonium thiocyanate solution.

Subst., I, 0.7612; II, 0.6391; cc. 0.1 *N* NH_4SCN, I, 13.66; II, 11.43.

Calc. for $C_{18}H_{14}O_4NCl_4Ag$: Ag, 19.34. Found: Ag, I, 19.36; II, 19.29.

Methyl Ester of the Tetrachloro Acid.—Fifteen grams of the tetrachloro acid were heated to boiling for 9 hours with 300 cc. of a 3% solution of dry hydrochloric acid gas in absolute methyl alcohol. On cooling, the solution was poured into its own volume of water. The ester separated as an amorphous body, which gradually became granular. It was purified by crystallization from ether. The ester has a very faint yellow color and melts at 146–148° to a clear yellow liquid. As the substance on being heated to even 100°, showed signs of decomposition, the analyses were made on the air-dried material.

Subst., I, 0.2267; II, 0.2142; cc. 0.1 *N* $AgNO_3$, I, 19.56; II, 18.47.
Calc. for $C_{18}H_{14}NO_4Cl_4CH_3$: Cl, 30.50. Found: Cl, I, 30.60; II, 30.57.

The methyl ester shows an extraordinary solubility, being soluble in methyl alcohol, ethyl alcohol, ether, benzene, toluene, chloroform, carbon tetrachloride, acetone and ethyl acetate.

Ethyl Ester of the Tetrachloro Acid.—The preparation was exactly analogous to that of the methyl ester, using a 3% solution of dry hydrochloric acid gas in ethyl alcohol. The ethyl ester was purified by crystallization from ether and is very like the methyl ester in its appearance and solubilities. It melts at 120° to a clear yellow liquid. Analyses of the air-dried material gave the following results:

Subst., I, 0.1992; II, 0.2125; cc. 0.1 *N* $AgNO_3$, I, 16.66; II, 17.83.
Calc. for $C_{18}H_{14}NO_4Cl_4C_2H_5$: Cl, 29.61. Found: Cl, I, 29.65; II, 29.75.

Acetylation Products of the Tetrachloro Acid.—Ten grams of the tetrachloro acid were heated with 70 g. of acetic anhydride for 7 hours on a boiling water bath. Previous experiments had shown that two products were formed, one of which is changed by boiling with alcohols. With this in mind, part of the solution was poured into a well cooled mixture of equal parts of acetone and water and the whole vigorously shaken. The acetylation products separated as a yellowish brown precipitate. This was dissolved in acetone and precipitated by the addition of water. This procedure was repeated until the substance was obtained free from the odor of acetic anhydride. It was dissolved in ether, the solution boiled for 10 minutes with boneblack and filtered, giving a bright yellow solution. From this, after repeated fractional crystallization, there was obtained a small quantity of a white product melting at 230–231°, and which analyses showed to be a diacetate of the tetrachloro acid.

Subst., I, 0.1585; II, 0.1643; cc. 0.1 *N* $AgNO_3$, I, 11.86; II, 12.26.
Calc. for $C_{18}H_{13}NO_4Cl_4(COCH_3)_2$: Cl, 26.51. Found: Cl, I, 26.53; II, 26.47.

There was also obtained a much larger amount of a pale yellow product, melting at 174–180° and which was also a diacetate of the tetrachloro acid.

Subst., I, 0.2143; II, 0.2780; cc. 0.1 *N* $AgNO_3$, I, 16.03; II, 20.79.
Calc. for $C_{18}H_{13}NO_4Cl_4(COCH_3)_2$: Cl, 26.51. Found: Cl, I, 26.52; II, 26.52.

Methyl and Ethyl Esters of the Monoacetate of the Tetrachloro Acid.—The remainder of the acetic anhydride solution was poured into absolute ethyl alcohol. Grayish white crystals separated on standing, which on crystallization from ether, gave a pale yellow product which melted at 174–180° and was identical with the yellow diacetate. The filtrate was boiled to convert the acetic anhydride into ethyl acetate and from this solution, after repeated fractional crystallization, two substances were obtained, one, a white product in very small amount, melting at 230–231°, identical with the white diacetate; the other in larger amount, a yellow substance, melting at 190–192°, and which analyses showed to be the ethyl ester of the monoacetate of the tetrachloro acid.

Subst., I, 0.1999; II, 0.1872; cc. 0.1 *N* $AgNO_3$, I, 15.42; II, 14.41.

Calc. for $C_{18}H_{13}NO_4Cl_4(COCH_3)(C_2H_5)$: Cl, 27.22. Found: Cl, I, 27.35; II, 27.29.

Two portions of the pale yellow product, melting at 174–180°, were boiled for 6 hours, one with ethyl alcohol and the other with methyl alcohol. From the ethyl alcohol solution, a yellow product was obtained melting at 190–192° and identical with the ethyl ester of the monoacetate. The methyl alcohol solution gave a yellow product melting at 152–155° and which analyses showed to be the methyl ester of the monoacetate of the tetrachloro acid.

Subst., I, 0.1888; II, 0.1940; cc. 0.1 *N* $AgNO_3$, I, 14.90; II, 15.32.

Calc. for $C_{18}H_{13}NO_4Cl_4(COCH_3)(CH_3)$: Cl, 27.98. Found: Cl, I, 27.98; II, 28.00.

The pale yellow product melting at 174–180° is therefore an acetate of a mixed anhydride similar to the one obtained by Haller and Umbgrove (page 2102). The white product melting at 230–231° undergoes no change when boiled with alcohols and is undoubtedly a true diacetate of the tetrachloro acid (page 2116).

Both the white and yellow acetylation products gradually dissolve in 2% aqueous potassium hydroxide solution. This shows that they are gradually saponified and go into solution as the yellow potassium salt of the tetrachloro acid. On longer standing, an atom of chlorine is removed, and the salt of the trichloro acid (page 2111) precipitates.

Both of the acetylation products are readily soluble in methyl alcohol, ethyl alcohol, benzene, chloroform, carbon tetrachloride, acetone, ethyl acetate and ether.

Action of Dry Hydrochloric Acid Gas on the Tetrachloro Acid.—A known weight of the dry tetrachloro acid was treated with dry hydrochloric acid gas. It rapidly increased in weight becoming constant at the end of 3 hours and absorbing an amount of hydrochloric acid corresponding to slightly more than one molecule when it was colorless.

Subst., 0.3308; gain, HCl, 0.0280.

Calc. for $C_{18}H_{15}O_4NCl_4.HCl$: HCl, 7.48. Found: HCl, 7.80.

When exposed to dry air it quickly loses most of its hydrochloric acid, finally returning to its original weight in about 20 hours. When the excess of hydrochloric acid over one molecule is lost, the substance changes to a light yellow.

Action of Dry Hydrochloric Acid Gas on the Methyl Ester of the Tetrachloro Acid.—When this compound is treated with dry hydrochloric acid gas, it rapidly takes up two molecules and the dihydrochloride formed is colorless.

Subst., 0.3458; gain, HCl, 0.0542.

Calc. for $C_{19}H_{17}O_4NCl_4.2HCl$: HCl, 13.56. Found: HCl, 13.55.

When this is placed in dry air it quickly loses one molecule of hydrochloric acid and changes to a pale yellow. The second molecule of hydrochloric acid is lost very slowly, in fact at the end of 14 days the substance still retained nearly 3% of hydrochloric acid.

Action of Dry Hydrochloric Acid Gas on the Methyl Ester of the Monoacetate of the Tetrachloro Acid.—When this substance is placed in dry hydrochloric acid gas, it quickly takes up more than two molecules and becomes colorless.

Subst., 0.2802; gain, HCl, 0.0439.

Calc. for $C_{21}H_{19}NO_5Cl_4.2HCl$: HCl, 12.27. Found: HCl, 13.54.

The dihydrochloride in dry air gradually loses weight and becomes constant, holding one molecule of hydrochloric acid at room temperature. The monohydrochloride is light yellow in color.

Potassium Salt of the Trichloro Acid.—This salt was prepared by dissolving the tetrachloro acid in aqueous 3% potassium hydroxide and heating the solution to boiling by passing in steam, when the yellow potassium salt of the trichloro acid separated. It crystallizes from methyl alcohol in bright yellow needles which melt at 285° to a pale red liquid. When crystallized from ethyl alcohol it had the same melting point. The crystals, from both methyl alcohol (I) and ethyl alcohol (II) contain two molecules of water of crystallization. This was shown by making potassium determinations on the air-dried product from the two solvents and also by determining the loss in weight on heating. A weighed quantity of the salt was dissolved in boiling water, an excess of standard hydrochloric acid added, the trichloro acid filtered off and the excess of hydrochloric acid titrated with standard sodium hydroxide solution.

Subst., I, 0.8536; II, 0.5652; cc. 0.1 *N* HCl, I, 17.36; II, 11.95.

Calc. for $C_{18}H_{13}NO_4Cl_3K.2H_2O$: K, 8.00. Found: K, I, 7.95; II, 8.27.

Loss in weight at 160°:

Subst., I, 0.4433; II, 0.5278; loss, I, 0.0374; II, 0.0422.

Calc. for $C_{18}H_{13}NO_4Cl_3K.2H_2O$: H_2O, 7.37. Found: H_2O, I, 8.44; II, 8.00.

Drops of water collected on the cool end of the drying tube in both determinations.

The dried product was analyzed for chlorine, nitrogen, and potassium.

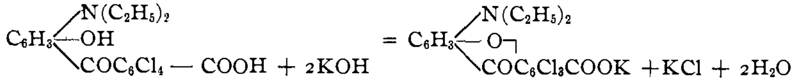
Subst., I, 0.2967; II, 0.2434; cc. 0.1 *N* $AgNO_3$, I, 19.75; II, 16.18.

Subst., I, 0.4926; II, 0.5872; cc. 0.1 *N* HCl, I, 11.21; II, 12.83.

Subst., I, 0.5468; II, 0.6321; cc. 0.1 *N* HCl, I, 12.17; II, 14.03.

Calc. for $C_{18}H_{13}NO_4Cl_3K$: Cl, 23.51; N, 3.10; K, 8.64. Found: Cl, I, 23.60; II, 23.57; N, I, 3.19; II, 3.06; K, I, 8.70; II, 8.68.

As it has already been shown that one atom of chlorine is removed from the tetrachloro acid by the potassium hydroxide (page 2108), the reaction is probably as follows (page 2118):



$$C_6H_3\begin{cases}N(C_2H_5)_2\\ OH\\ COC_6Cl_4-COOH\end{cases} + 2KOH = C_6H_3\begin{cases}N(C_2H_5)_2\\ O\urcorner\\ COC_6Cl_3COOK\end{cases} + KCl + 2H_2O$$

This potassium salt is soluble in methyl alcohol, ethyl alcohol, glacial acetic acid; slightly soluble in acetone, benzene and ether. It is quite soluble in hot water, from which it is precipitated by a solution of potassium hydroxide. This product loses weight when heated to 160° corresponding to three molecules of water of crystallization.

Subst., 0.9203; loss, H_2O, 0.1017.
Calc. for $C_{18}H_{13}NO_4Cl_3K.3H_2O$: H_2O, 10.67. Found: H_2O, 11.05.

Trichlorodiethylaminoxanthonecarboxylic Acid.—This compound was made by dissolving the potassium salt described above in boiling water, and adding hydrochloric acid to the solution. The trichloro acid separates as an amorphous mass. It crystallizes from methyl alcohol in bright yellow needles which melt at 278° to a pale red liquid. It also crystallizes from ethyl alcohol in bright yellow needles melting at 278°, but which contain *no solvent of crystallization.* The product from methyl alcohol, when heated to 160°, rapidly comes to constant weight, no moisture collects on the cool end of the drying tube and the loss is equivalent to exactly one molecule of methyl alcohol.

Subst., 1.1912; loss, CH_3OH, 0.0857.
Calc. for $C_{18}H_{14}NO_4Cl_3.CH_3OH$: CH_3OH, 7.19. Found: CH_3OH, 7.17.

The residue when analyzed for chlorine and nitrogen proved to be the trichloro acid (page 2118).

Subst., I, 0.2006; II, 0.2370; cc. 0.1 *N* $AgNO_3$, I, 14.51; II, 17.16.
Subst., I, 0.6437; II, 0.7126; cc. 0.1 *N* HCl, I, 15.80; II, 16.94.
Calc. for $C_{18}H_{14}NO_4Cl_3$: Cl, 25.66; N, 3.38. Found: Cl, I, 25.65; II, 25.68; N, I, 3.44; II, 3.33.

To determine whether the acid is precipitated from a solution of its potassium salt as the trichloro acid or as a hydrate of this acid (page 2118) some of the powdered salt was suspended in cold water, concentrated hydrochloric acid added and the mixture thoroughly shaken to coagulate the trichloro acid set free. This was filtered off and washed with water until free from hydrochloric acid. At the same time, some of the potassium salt was dissolved in boiling water and the trichloro acid precipitated from this solution by the addition of concentrated hydrochloric acid. Moisture determinations were made on the two air-dried products:

Subst., I, 0.4151; II, 0.3867; loss, H_2O, I, 0.0104; II, 0.0176.
Calc. for $C_{18}H_{14}NO_4Cl_3.H_2O$: H_2O, 4.16. Found: H_2O, I, 2.50; II, 4.55.

(I) was made on the trichloro acid precipitated from the boiling solution, while (II) was made on the acid precipitated cold. The heating was begun at 115° and at the end of each hour the material was weighed, returned to the drying tube and the temperature increased until the final heating was at 175°. In (I), the substance lost no weight after heating for one hour at 115°, while in the other case it was heated for one and one-half hours at 115° and one hour at 140° before it reached constant weight. In neither case did any moisture collect on the cool end of the drying tube. These results show that the acid precipitated in the cold from its potassium salt is obtained as the hydrate (page 2118), which readily loses a molecule of water of constitution and that it loses part of this water when precipitated out of a boiling solution of the salt with acids.

The trichloro acid is soluble in methyl alcohol, ethyl alcohol and glacial acetic acid, less soluble in acetone; insoluble in water. It is very stable toward alkalies, no chlorine being removed even when it is boiled with alcoholic caustic potash. It is highly probable that the yellow product obtained by Bloch (page 2104) is the trichloro*dimethyl*aminoxanthonecarboxylic acid.

Action of Dry Ammonia Gas on the Dried Trichloro Acid.—When a weighed quantity of the trichloro acid, dried at 160°, is treated with dry ammonia gas it rapidly absorbs more than one molecule of ammonia with no noticeable change of color.

Subst., 0.7068; gain, NH_3, 0.0406.

Calc. for $C_{18}H_{14}NO_4Cl_3.NH_3$: NH_3, 3.95. Found: NH_3, 5.43.

This compound, when exposed to dry air, loses its excess of ammonia over one molecule very rapidly. The monoammonium salt left is hygroscopic but stable.

Action of Acetic Anhydride on the Trichloro Acid.—Ten grams of the trichloro acid were boiled for 3 hours with 70 g. of acetic anhydride. On cooling, a product separated which was filtered off, washed with cold absolute alcohol and air-dried. It crystallizes in bright yellow needles, melts at 188–190°, with slight decomposition and on drying at 120°, loses no appreciable weight. Analyses on the dried product gave the following results:

Subst., I, 0.1902; II, 0.1686; cc. 0.1 *N* $AgNO_3$, I, 12.52; II, 11.12.

Calc. for $C_{18}H_{13}NO_4Cl_3(COCH_3)$: Cl, 23.30. Found: Cl, I, 23.34; II, 23.39.

The yellow acetate is soluble in acetic anhydride, methyl alcohol, ethyl alcohol, acetone and benzene; insoluble in water. When crystallized from acetone, a yellow powder is obtained which melts very indefinitely at about 185°. This was heated at 155–160° for 25 hours before it reached constant weight and showed a loss of 11.20%. A current of dry air was passed over the compound while it was being heated and on leaving the drying tube this current of air was led through a gas wash bottle containing distilled water. After the compound had reached constant weight, the water in this wash bottle gave a strong iodoform test for acetone. The product after heating melts at 278°, the melting point of the trichloro acid.

Subst., 0.5428; loss, acetone, 0.0608.
Calc. for $C_{18}H_{14}NO_4Cl_3(C_3H_6O)$: acetone, 12.28. Found: acetone, 11.20.

Hence, the acetate when crystallized from acetone forms an acetonate of the trichloro acid (page 2119).

A portion of the yellow acetate was boiled with ethyl alcohol for six hours and the solution cooled. A product separated in the form of bright yellow needles, melting at 278°, the melting point of the trichloro acid. On drying at 160°, this material lost no weight.

The product obtained by the action of acetic anhydride on the trichloro acid is therefore a mixed anhydride rather than a true acetate (pages 2102, 2118).

Attempts to make the methyl ester of the trichloro acid by the catalytic method of esterification resulted in failure. This is in accord with the fact that the acetyl group is removed from the mixed anhydride when it is boiled with ethyl alcohol but the product formed is the free acid and not the ester.

Action of Dry Hydrochloric Acid Gas on the Dry Trichloro Acid.—A weighed amount of dry trichloro acid was treated with dry hydrochloric acid gas. At the end of three hours it showed no change in appearance and had absorbed only 0.3% of hydrochloric acid. When concentrated hydrochloric acid is added to the trichloro acid, it does not go into solution, but turns white. This white hydrochloride when filtered off and dried in the air loses hydrochloric acid as it dries, and turns yellow.

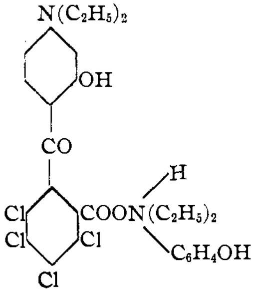
Action of Dry Hydrochloric Acid Gas on the Mixed Anhydride of the Trichloro Acid and Acetic Acid.—The mixed anhydride dried at 120° absorbs one molecule of hydrochloric acid gas in two hours and has a pale yellow color. At the end of six hours it reaches constant weight, having absorbed more than one molecule and is colorless.

Subst., 0.4016; gain, HCl, 0.0414.
Calc. for $C_{20}H_{16}NO_5Cl_3.HCl$: HCl, 7.40. Found: HCl, 9.35.

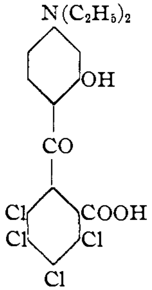
The hydrochloride loses all its hydrochloric acid on standing over night at room temperature in dry air.

Theoretical.

Hydroxyphenyldiethylammonium - diethylamino - *m* - hydroxybenzoyltetra-chlorobenzoate is the product resulting from the condensation of diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride under such conditions that tetrachlororhodamine formation does not take place. It seems highly probable that the reaction proceeds in two stages (page 2106), and that the tetrachloro acid is first formed. However, *the final product* is always the substituted ammonium salt of the tetrachloro acid, whether the condensation is brought about in toluene solution or by direct heating of the two components.

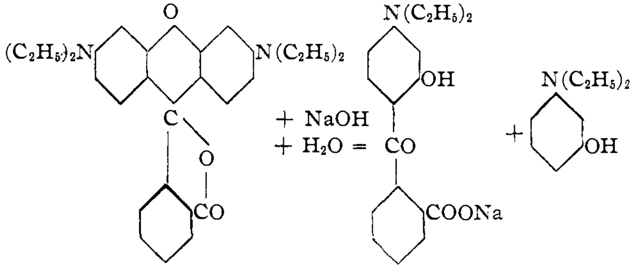


(I).



(II).

Formula (I) for this salt explains the readiness with which it is decomposed into the tetrachloro acid, (II) and diethyl-*m*-aminophenol by the action of alkalies and mineral acids and also the color of the compound. That the ketone group occupies the *ortho* position to the hydroxyl, follows from the ease with which the tetrachloro acid is converted into the trichloro acid by weak alkalies (page 2111) and also from the color of the compound, Staedel[1] having shown that the *ortho*hydroxybenzophenones are yellow. That the diethylamino group is in the *para* position is proved by the fact that the tetrachloro acid is so readily converted into tetrachlororhodamine.[2] The decomposition of tetraethylrhodamine into *p*-diethylamino-*m*-hydroxybenzoyl-*o*-benzoic acid (page 2102) and diethyl-*m*-aminophenol:



is also in accord with the above view of the structure of the tetrachloro acid.

Like the phthaleins, the tetrachloro acid yields derivatives of a tautomeric form such as the diacetate and the free acid may be a mixture of this form (II) with the ketone form (I) (page 2116).

When the tetrachloro acid is treated with dry ammonia, it first forms the true ammonium salt, and then absorbs a second molecule of ammonia

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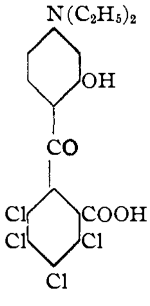
[1] *Ann.*, **283**, 175 (1894).

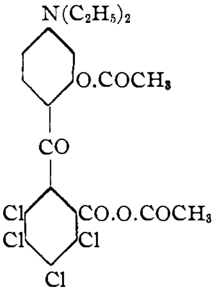
[2] *Bull. soc. chim.*, **25**, 747 (1901).

to neutralize the phenol hydroxyl group. This diammonium salt loses the molecule of ammonia absorbed by the hydroxyl group very readily in dry air at room temperature giving a stable monoammonium salt. This behavior is evidence of the strong acid character of the molecule. The fact that the tetrachloro acid forms esters so readily by the catalytic method of esterification, unlike the tetrachloro acid of Haller and Umbgrove (page 2102), is worthy of note, since it forms an exception to the Victor Meyer rule.

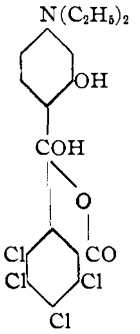
The behavior of the tetrachloro acid with acetic anhydride shows that it acts as a tautomeric substance.



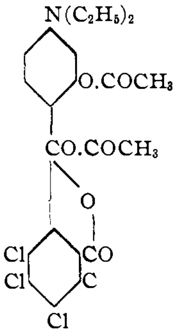
(I).



Yellow.



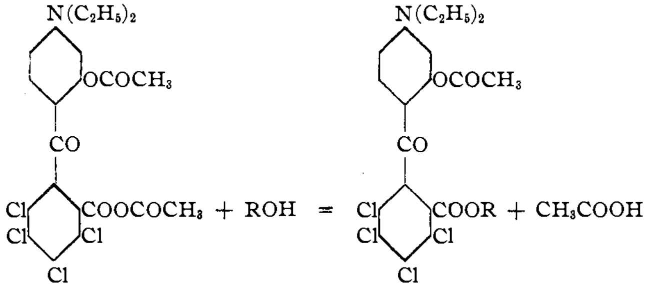
(II).



Colorless.

The yellow product, melting at 174–180° is a derivative of Formula (I), while the colorless product melting at 230–231° is a derivative of Formula (II).

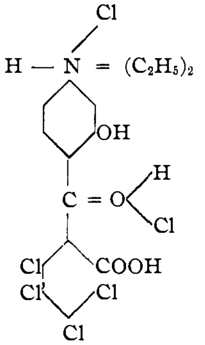
That the yellow product has the formula assigned to it is confirmed by its forming esters of the monoacetate when boiled with alcohols according to the equation



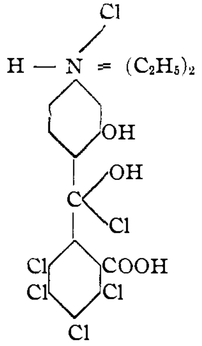
It is not then a true diacetate of the tetrachloro acid, but the monoacetate of the mixed anhydride of the tetrachloro acid and acetic acid as shown above.

Its color is probably due to the ketone group connected with the two benzene residues as in the case of the tetrachloro acid. The white product is a true diacetate of the tetrachloro acid, as it is not changed by boiling with alcohols and has no color. The absence of color is due to the fact that the ketone group is no longer present.

The behavior of the tetrachloro acid toward dry hydrochloric gas shows its basic nature. It absorbs more than one molecule, but loses the excess quite readily in dry air at room temperature. The monohydrochloride is yellow while the salt containing an excess of hydrochloric acid is colorless. The excess of hydrochloric acid may be absorbed by the ketone group, forming an oxonium salt or a carbonium salt.



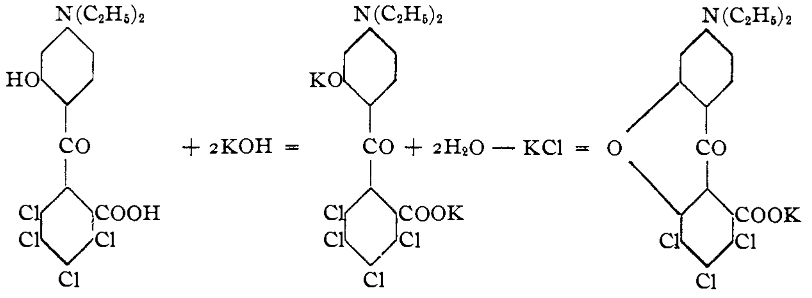
Oxonium salt.



Carbonium salt.

Both formulas show why the salt having an excess of hydrochloric acid is colorless, as both in the oxonium salt and in the carbonium salt the ketone group is no longer present. The hydrochloric acid absorbed by the ketone group is the first to be lost in dry air and the yellow color returns. When the acid group is neutralized by a methyl or ethyl radical, the ester forms a dihydrochloride which is colorless for the same reason that the tetrachloro acid containing an excess of hydrochloric acid is colorless. It is not until the phenol hydroxyl group as well as the carboxyl group is neutralized that a hydrochloride stable at room temperature is formed. The methyl ester of the monoacetate of the tetrachloro acid absorbs two molecules of hydrochloric acid and the dihydrochloride is colorless. It loses one molecule of its hydrochloric acid at room temperature and the monohydrochloride is yellow and stable.

The removal of chlorine from the tetrachloro acid by even such weak alkaline solutions as ammonium hydroxide and sodium carbonate is of special interest as it is the first case of its kind to be noticed in this laboratory where the tetrachloro compounds have received considerable attention. As the alkali salts do not precipitate from 10% solutions of the caustic alkalies until the solutions are diluted or heated, it is very probable that the reaction in which the chlorine is removed takes place in stages as follows:



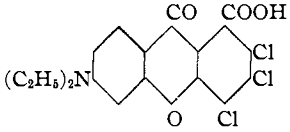
Soluble. Insoluble in alkalies.

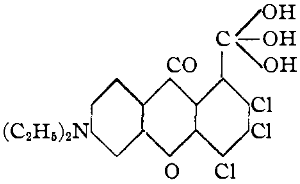
The fact that the salt of the trichloro acid and the acid itself are much more *highly colored* than the corresponding tetrachloro compounds is also in accord with this view, as ring formation is frequently attended with an increase of color.

The free trichloro acid is readily obtained by decomposing its salts with mineral acids. It is precipitated from its potassium salt in the cold as a hydrate (page 2112), while from a boiling solution it is obtained nearly anhydrous.

It is rather curious that it should crystallize from methyl alcohol with a molecule of methyl alcohol, while it crystallizes from ethyl alcohol with no solvent of crystallization. This is probably due to the fact that methyl alcohol is more nearly like water in its properties than is ethyl alcohol.

The trichloro acid and its hydrate are hence derivatives of xanthone and have the following structures:

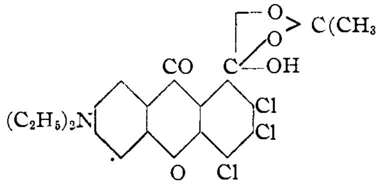




The name of the acid is, therefore, 2,3,4-trichloro-6-diethylamino-xanthone-1-carboxylic acid.

Like the tetrachloro acid, the trichloro acid combines with dry ammonia to form a monoammonium salt which is stable at room temperature.

There being no hydroxyl groups present in the molecule, the trichloro acid reacts with acetic anhydride to form a mixed anhydride (page 2113) as in the case of the acid obtained by Haller and Umbgrove (page 2102). This mixed anhydride is very unstable as is shown by the fact that the acetyl group is removed by boiling with ethyl alcohol and the acid is set free instead of ester formation taking place. The acetonate of the trichloro acid formed when the mixed anhydride is boiled with acetone probably has the following structure:



The fact that the trichloro acid does not form a methyl ester by the catalytic method of esterification is probably due to steric hindrance.

The trichloro acid does not absorb hydrochloric acid gas as the diethylamino group is here neutralized by the carboxyl group. When the hydrogen atom of this carboxyl group is replaced by an acetyl group the mixed anhydride absorbs more than one molecule of hydrochloric acid and is colorless. The excess of hydrochloric acid is probably taken up in this case by the ketone group forming an oxonium or a carbonium salt as in the case of the hydrochlorides of the tetrachloro compounds.

Summary.

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

1. The condensation of diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride has been effected in both an indifferent solution medium and by the direct heating of a mixture of the two components. The result of the condensation is always hydroxyphenyldiethylammonium-diethylamino-*m*-hydroxybenzoyl-tetrachlorobenzoate.
2. The tetrachloro acid has been prepared by decomposing the substituted ammonium salt first formed with mineral acids or alkalies.
3. The ammonium and silver salts, the methyl and ethyl esters, the acetate of the mixed anhydride of the tetrachloro acid and acetic acid, and the methyl and ethyl esters of the monoacetate of the tetrachloro acid have been prepared. All these compounds are colored and are derivatives of the keto-form of the tetrachloro acid.
4. A white diacetate has been prepared. This is a derivative of the tautomeric lactoid form of the tetrachloro acid.
5. The action of dry hydrochloric acid gas on the tetrachloro acid, its methyl ester and the methyl ester of its monoacetate has been studied.
6. One atom of chlorine has been removed from the tetrachloro acid together with an atom of hydrogen and the resulting trichloro acid, a xanthone derivative, has been obtained and studied.
7. The potassium and ammonium salts of the trichloro acid, the acetonate of the trichloro acid and the mixed anhydride of the trichloro acid and acetic acid have been prepared.
8. The action of dry hydrochloric acid gas on the trichloro acid and on the mixed anhydride of the trichloro acid and acetic acid, has been studied.

ITHACA, N. Y