

the action of formaldehyde vapor upon the magnesium bromide derivatives of the corresponding acetylenes.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]
**ORTHO-CRESOL-TETRACHLOROPHTHALEIN, SOME OF ITS
DERIVATIVES, AND ISO-ORTHO-CRESOL-
TETRACHLOROPHTHALEIN**

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Ortho-cresol-tetrachlorophthalein was first made in this Laboratory by E. L. Arnold² from tetrachlorophthalic acid and *o*-cresol, using stannic chloride as the condensing agent. For making larger quantities of the phthalein, fuming sulfuric acid proved to be a better condensing agent. A mixture of 100 g. of *pure* crystallized tetrachlorophthalic acid and 200 g. of *pure o*-cresol was heated until water ceased to be evolved and all the acid was converted into the anhydride; 55 cc. of 15% fuming sulfuric acid was then added and the mixture heated at 140° for ten hours. Water was added and the unused *o*-cresol removed by distillation in steam. The residue was boiled repeatedly with water to remove soluble products, the crude phthalein dissolved in 5% sodium hydroxide solution, the solution filtered to remove dimethyl tetrachlorofluoran and the filtrate acidified; 135 g. of the crude phthalein was obtained, an 84% yield. The phthalein was crystallized from methanol, the solution being decolorized with bone-black. After recrystallization from methanol it was analyzed.

Anal. Subs., 0.1607, 0.1239, 0.1437: AgCl, 0.1890, 0.1476, 0.1705. Calcd. for C₂₂H₁₄O₄Cl₄: Cl, 29.32. Found: 29.10, 29.47, 29.35.

The chemical and physical properties of *o*-cresol-tetrachlorophthalein were found to be the same as those given by Arnold.²

ITS DIACETATE was made by the method given by Arnold.² It was crystallized from methanol until it was colorless; m. p., 207–208°.

Anal. Subs., 0.2849, 0.2750: AgCl, 0.2857, 0.2769. Calcd. for C₂₂H₁₂O₂Cl₄-(OCOCH₃)₂: Cl, 24.97. Found: 24.81, 24.91.

THE DIBENZOATE was made by heating the pure phthalein with benzoyl chloride. It was crystallized from ethanol until it was colorless; m. p., 198–200°.

Anal. Subs., 0.2015, 0.2056: 11.70, 11.90 cc. of 0.1 N AgNO₃. Calcd. for C₂₂H₁₂-O₂Cl₄(OCOC₆H₅)₂: Cl, 20.49. Found: 20.59, 20.53.

The dibenzoate is readily soluble in benzene, toluene, xylene, acetone and ethyl acetate. It is less soluble in methanol, ethanol and ether.

Dibromo-*o*-cresol-tetrachlorophthalein.—Ten g. of pure *o*-cresol-tetrachlorophthalein was dissolved in 500 cc. of absolute alcohol and 9 g.

¹ From a dissertation presented by M. S. Patel in partial fulfilment of the requirements for the degree of Master of Science.

² Arnold, *THIS JOURNAL*, **46**, 489 (1924).

of bromine added drop by drop. On standing, crystals of the dibromo compound separated. These were crystallized from methanol until colorless; m. p., 270–271°.

*Anal.*³ Subs., 0.2668, 0.2545: 24.95, 23.80 cc. of 0.1 *N* AgNO₃; Ag Hal., 0.3944, 0.3763. Calcd. for C₂₂H₁₂O₄Cl₄Br₂: Cl, 22.11; Br, 24.90. Found: Cl, 22.17, 22.13; Br, 24.77, 24.81.

Dibromo-*o*-cresol-tetrachlorophthalein dissolves readily in warm ethanol and is soluble in methanol, acetone and acetic acid. In dilute solutions of the alkalis it dissolves with the development of a light blue color while in concd. solutions the color is a dark purplish-blue. The end-point (colorless to blue) is between *P_H* 7.2 and *P_H* 7.6.

DIAMMONIUM SALT.—The dibromo compound absorbs two molecules of dry ammonia gas and turns dark blue. On allowing the salt to stand in the air, it loses its color owing to the loss of ammonia and on heating it to 80° the original weight of the colorless dibromophthalein is obtained.

Anal. Subs., 0.2344: NH₃, 0.0122. Calcd. for C₂₂H₁₂O₄Cl₄Br₂(NH₃)₂: NH₃, 5.04. Found: 4.97.

DISILVER SALT.—The disodium salt was first made by the action of sodium ethylate on the dibromophthalein dissolved in alcohol. This solution was evaporated to dryness on a steam-bath, the blue disodium salt dissolved in water and a solution of silver nitrate added in slight excess. The silver salt of the dibromophthalein precipitated as a light blue, flocculent mass. It was filtered off, washed free from silver nitrate and dried to constant weight in a vacuum desiccator over concd. sulfuric acid. A weighed quantity was oxidized with aqua regia and the silver chloride formed was weighed.

Anal. Subs., 0.4216, 0.3840: AgCl, 0.1400, 0.1292. Calcd. for C₂₂H₁₀O₄Cl₄Br₂Ag₂: Ag, 25.22. Found: 24.94, 25.32.

DIACETATE.—This was made in the same way as the diacetate of *o*-cresol-tetrachlorophthalein. It was crystallized from methanol. The colorless crystals melt at 237–239°.

Anal. Subs., 0.3164, 0.2732: 26.15, 22.60 cc. of 0.1 *N* AgNO₃; Ag Hal., 0.4134, 0.3571. Calcd. for C₂₂H₁₀O₂Cl₄Br₂(OCOCH₃)₂: Cl, 19.54; Br, 22.02. Found: Cl, 19.59, 19.66; Br, 21.91, 21.82.

The diacetate is soluble in benzene, glacial acetic acid, acetone and xylene. It is less soluble in methanol and ethanol. It dissolves in concd. sulfuric acid, forming a red solution and undergoing saponification. It is also readily saponified by an alcoholic solution of potassium hydroxide.

DIBENZOATE.—This was made in the same way as the dibenzoate of *o*-cresol-tetrachlorophthalein. It was crystallized from benzene by the addition of acetone. It is colorless; m. p., 176–178°.

Anal. Subs., 0.3258, 0.3360: 22.90, 23.70 cc. of 0.1 *N* AgNO₃; Ag Hal., 0.3624, 0.3750. Calcd. for C₂₂H₁₀O₂Cl₄Br₂(OCOC₆H₅)₂: Cl, 16.69; Br, 18.80. Found: Cl, 16.56, 16.62; Br, 18.84, 18.88.

The dibenzoate is very soluble in xylene, benzene and toluene, and only slightly soluble in methanol and ethanol.

³ See Orndorff and Black, *Am. Chem. J.*, **41**, 349 (1909) for method of computing chlorine and bromine.

DIMETHYL ETHER.—This was made by boiling a solution of the disodium salt (made by the action of sodium methylate on a methyl alcoholic solution of the dibromophthalein) with methyl iodide and filtering off the dimethyl ether from time to time. It was purified by extracting it with boiling sodium hydroxide solution and crystallizing the residue from acetone.

Anal. Subs., 0.2862, 0.2585: 25.65, 23.20 cc. of 0.1 *N* AgNO₃; Ag Hal., 0.4054, 0.3669. Calcd. for C₂₂H₁₀O₄Cl₄Br₂(CH₃)₂: Cl, 21.17; Br, 23.86. Found: Cl, 21.25, 21.21; Br, 23.68, 23.82.

The dimethyl ether is soluble in benzene, acetone and glacial acetic acid. It is only slightly soluble in methanol and ethanol. It is colorless and insoluble in aqueous alkalis, but dissolves in a boiling alcoholic solution of potassium hydroxide without development of color; m. p., 245–247°.

DIETHYL ETHER.—This was made in the same way as the dimethyl ether, using absolute alcohol and ethyl iodide. It was purified in the same way as the dimethyl ether and then crystallized from methanol.

Anal. Subs., 0.3278, 0.3098: 27.75, 26.30 cc. of 0.1 *N* AgNO₃; Ag Hal., 0.4391, 0.4158. Calcd. for C₂₂H₁₀O₄Cl₄Br₂(C₂H₅)₂: Cl, 20.32, Br, 22.90. Found: Cl, 19.97, 20.11; Br, 22.64, 22.54.

The diethyl ether is colorless and melts at 172–175°, with decomposition.

Dinitro-*o*-cresol-tetrachlorophthalein.—To 25 g. of pure *o*-cresol-tetrachlorophthalein suspended in 500 cc. of glacial acetic acid, 30 cc. of concd. sulfuric acid was added. This mixture was stirred mechanically and 20 cc. of concd. nitric acid added drop by drop. After stirring had been continued for 24 hours the dinitro product was filtered off, boiled with 500 cc. of ethanol to remove any unchanged *o*-cresol-tetrachlorophthalein, and the residue crystallized from acetone.

Anal. Subs., 0.2737, 0.2893: 19.10, 20.30 cc. of 0.1 *N* AgNO₃. Calcd. for C₂₂H₁₂O₆Cl₄N₂: Cl, 24.71. Found: 24.75, 24.88.

Subs., 0.4780, 0.4642: 17.00, 16.40 cc. of 0.1 *N* HCl. Calcd. for C₂₂H₁₂O₆Cl₄N₂: N, 4.88. Found: 4.98, 4.95.

Dinitro-*o*-cresol-tetrachlorophthalein is light yellow; m. p., 232–234°. It dissolves in solutions of the alkalis with the development of a yellow color. It is practically insoluble in methanol, ethanol and benzene, but is soluble in hot acetone.

Diacetate.—This was made in the same way as the diacetate of *o*-cresol-tetrachlorophthalein. It was crystallized from ethanol. The yellow crystals fused when heated to 140°, with the loss of a molecule of water.

Anal. Subs., 0.5692, 0.4230: loss at 140°, 0.0148, 0.0112. Calcd. for C₂₂H₁₀O₆Cl₄N₂(OCOCH₃)₂ + H₂O: H₂O, 2.67. Found: 2.60, 2.65.

Subs. (dried at 140°), 0.2608, 0.2940: 16.00, 18.10 cc. of 0.1 *N* AgNO₃. Calcd. for C₂₂H₁₀O₆Cl₄N₂(OCOCH₃)₂: Cl, 21.55. Found: 21.75, 21.83.

The anhydrous diacetate melts at 206–208°. The crystallized product is readily soluble in benzene, xylene and acetone. It is sparingly soluble in methanol and ethanol. It is insoluble in a cold 10% solution of sodium hydroxide, but is partially saponified when the mixture is boiled.

ACTION OF DRY AMMONIA ON DINITRO-*o*-CRESOL-TETRACHLOROPHTHALEIN.—The dinitro compound absorbs three molecules of ammonia and turns dark brown.

Anal. Subs., 0.3140: NH_3 , 0.0284. Calcd. for $\text{C}_{22}\text{H}_{12}\text{O}_8\text{Cl}_4\text{N}_2(\text{NH}_3)_3$: NH_3 , 8.17. Found: 8.29.

The ammonia is gradually lost on standing in the air and the last traces are removed when the product is heated to 100° . The original weight of the yellow dinitro-phthalein was recovered.

2' - Hydroxy - 3' - methylbenzoyl - 3,4,5,6 - tetrachloro - 2 - benzoic Acid.—This acid was made by the method of Ullmann and Schmidt.⁴ It was crystallized several times from glacial acetic acid and was finally obtained in light yellow crystals; m. p., $217\text{--}220^\circ$.

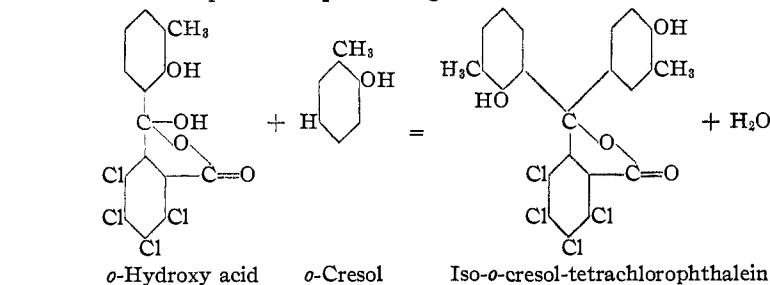
Anal. Subs., 0.2186, 0.2065: 22.40, 21.20 cc. of 0.1 *N* AgNO_3 . Calcd. for $\text{C}_{14}\text{H}_8\text{O}_4\text{Cl}_4$: Cl, 36.00. Found: 36.34, 36.40.

The acid is readily soluble in methanol, ethanol, glacial acetic acid, benzene and xylene. It dissolves in sodium hydroxide solution with the development of a bright yellow color.

Iso-*o*-cresol-tetrachlorophthalein.—Thirty g. of 2'-hydroxy-3'-methylbenzoyl-3-4-5-6-tetrachloro-2-benzoic acid was condensed with 16 g. of *o*-cresol, using 20 g. of stannic chloride as the condensing agent. The mixture was heated at 110° for eight hours. Dil. hydrochloric acid was then added and the unchanged *o*-cresol removed by steam distillation. The isophthalein was then extracted with 1% sodium hydroxide solution until the product formed by the addition of hydrochloric acid was colorless. It was dissolved in 2% sodium hydroxide solution, the blue solution thus obtained filtered, acidified and the product crystallized thrice from methanol.

Anal. Subs., 0.2900, 0.2918: 23.80, 24.10 cc. of 0.1 *N* AgNO_3 . Calcd. for $\text{C}_{22}\text{H}_{14}\text{O}_4\text{Cl}_4$: Cl, 29.32. Found: 29.10, 29.22.

Iso-*o*-cresol-tetrachlorophthalein is colorless and melts at $261\text{--}263^\circ$ with decomposition. It is readily soluble in methanol, ethanol, acetone and slightly soluble in ether and in benzene. In dilute solutions of the alkalis it dissolves with development of a blue color. The end-point lies between P_{H} 9.2 and P_{H} 9.6. It dissolves in concd. sulfuric acid forming a red solution, and water precipitates the isophthalein from this solution. The equation representing the reaction is as follows.



⁴ Ullmann and Schmidt, *Ber.*, **52**, 2098 (1919).

Summary

1. *o*-Cresol-tetrachlorophthalein, its diacetate and dibenzoate have been prepared. As these are *colorless* compounds they have the *lactoid* structure. In alkaline solutions the phthalein dissolves with the development of a *reddish-purple color* due to the formation of *quinoid* salts.

2. Dibromo-*o*-cresol-tetrachlorophthalein, its diacetate and dibenzoate and the dimethyl and diethyl ethers have been prepared. These are all *colorless* and have the *lactoid* structure. The dibromo-*o*-cresol-tetrachlorophthalein forms an unstable diammonium salt and a disilver salt. These salts are *blue* and are derived from the *quinoid* form of the dibromophthalein.

3. Dinitro-*o*-cresol-tetrachlorophthalein has been made. As in the case of the dibromo compound, it is probable that the two substituting groups take the *ortho* positions to the hydroxyl groups. The action of ammonia on the dinitro compound has also been studied. When acetylated the dinitro derivative gives a diacetate, which loses a molecule of water at 140°. This would seem to indicate that the diacetate has the carbinol carboxylic acid structure.

4. An isomer of *o*-cresol-tetrachlorophthalein has been made by first making 2'-hydroxy-3'-methyl-benzoyl-3,4,5,6-tetrachloro-2-benzoic acid by the condensation of *o*-cresol with tetrachlorophthalic acid anhydride and then condensing this acid with *o*-cresol. From the method of formation of this isomer, one hydroxyl group must be in the *ortho* position and the other in the *para* position to the methane carbon atom, while in the *o*-cresol-tetrachlorophthalein both the hydroxyl groups are in the *para* positions.

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VAPOR PRESSURES AND BOILING POINTS OF MONO- AND DIMETHYLANILINES AND MONO- AND DIETHYLANILINES

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There has been an ever-increasing demand for physical constants of organic compounds, particularly intermediates for dyes. The vapor pressures and boiling points of many of these compounds have been determined in the past by methods which afterwards were shown to be unreliable,¹ and the results obtained on the same compounds by different workers show in many cases considerable variations. The National Research Council, accordingly, requested that the vapor pressures and boiling

¹ Smith and Menzies, *THIS JOURNAL*, **32**, 1416 (1910).