[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# $3^1,3^2,3^3$-TRIMETHYL-AURIN (ORTHO-CRESAURIN) AND $3^1,3^2,3^3$-TRIMETHYL-$N^1,N^2,N^3$-TRIPHENYL-PARA-ROSANILINE (TRIPHENYL-ROS-ORTHO-TOLUIDINE)

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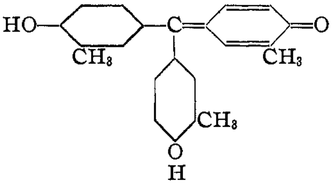
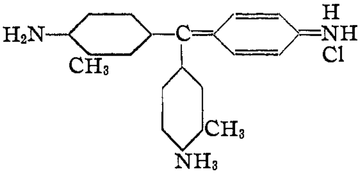
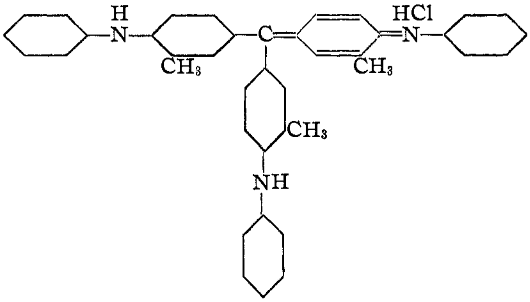
If the condensation between *o*-cresol and carbon tetrachloride be analogous to that between phenol and carbon tetrachloride,[3] then at least eight different compounds might be expected to result. Of these, only two have been described in the literature, and they were obtained in reactions quite different from the one suggested above. Shortly after this work was begun, we found that one of these two substances did not possess the constitution assigned to it. While not all the various products which are formed in the mentioned condensation have been identified, we have gone far enough to be able to explain the course of this reaction and to show that it is analogous to that between phenol and carbon tetrachloride; and we have worked out in detail a practical method for the preparation of the chief product, namely, the dye, I. The constitution of this dye was definitely proved to be $3^1,3^2,3^3$-trimethyl-$4^1,4^2$-dihydroxyquino-methane.



$3^1,3^2,3^3$-trimethyl-aurin,
(*o*-Cresaurin)
I



$3^1,3^2,3^3$-trimethyl-*p*-rosaniline,
(Ros-*o*-toluidine)
II



$3^1,3^2,3^3$-trimethyl-$N^1,N^2,N^3$-triphenyl-*p*-rosaniline,
(Triphenyl-ros-*o*-toluidine)
III

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[1] The material here presented is from the dissertation submitted by L. C. Anderson to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.

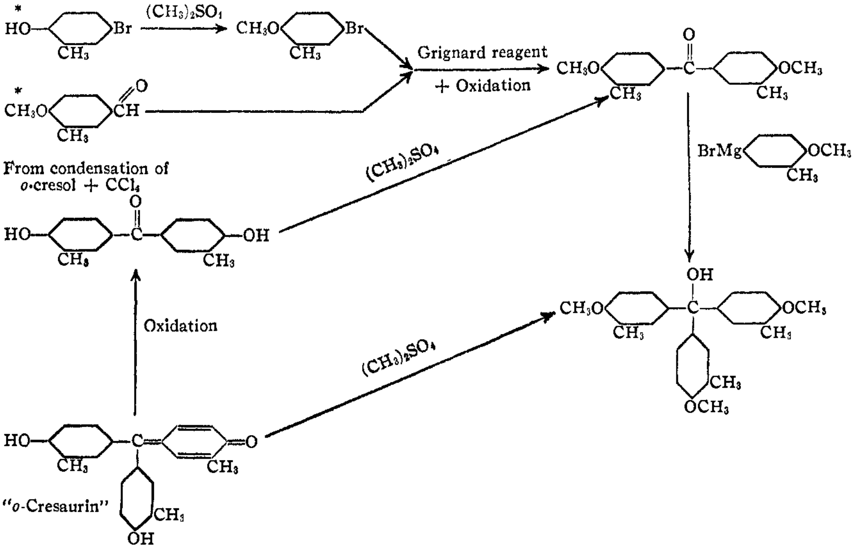
[2] The substance of this paper was presented before the Organic Section of the American Chemical Society at the 69th meeting of the Society at Baltimore, 1925.

[3] Gomberg and Snow, THIS JOURNAL, **47,** 198 (1925).

The conversion of this material into $4^1,4^2,4^3$-triarylamino-$3^1,3^2,3^3$-trimethyl-triphenyl-carbinol salts, hitherto unobtainable, has been realized. The following nomenclature of the main substances to be discussed in this paper is suggested in conformity with the naming of "*p*-rosaniline."

After our work had become well advanced, Baines and Driver[4] published a paper on the Reimer-Tiemann reaction. In the course of their work, they prepared corallins which contained aurin, $2^1,2^2,2^3$-trimethyl-aurin, or $3^1,3^2,3^3$-trimethyl-aurin, by the reaction between carbon tetrachloride and an alkaline phenolate, *m*-cresolate, or *o*-cresolate, respectively. In their detailed description of $3^1,3^2,3^3$-trimethyl-aurin, they state: "It was purified by recrystallization from 10% hydrochloric acid, being obtained in tufts of fine, red needles." In our experience, this procedure is not satisfactory for the purpose. No proof was advanced that they had the substance pure nor that it really was $3^1,3^2,3^3$-trimethylaurin, rather than one of the possible isomers. We have now proved, however, that their surmise was correct.

During the time that this paper was being written, C. H. Spiers[5] reported that he had prepared *o*-cresaurin from ros-*o*-toluidine ("New Fuchsin") by the diazo reaction. No decisive proof is offered for the constitution of the commercial product marked "New Fuchsin" and consequently the constitution of their *o*-cresaurin remained still undecided.[6]



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[4] Baines and Driver, *J. Chem. Soc.*, **123**, 1214 (1923).

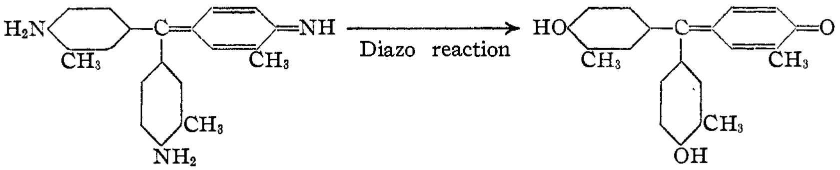
[5] Spiers, *ibid.*, **125**, 450 (1924).

[6] Spiers states that he started with *triaminotritolylmethane base.* We assume that he meant color base or carbinol, since at no step in his work does he oxidize a leuco base.

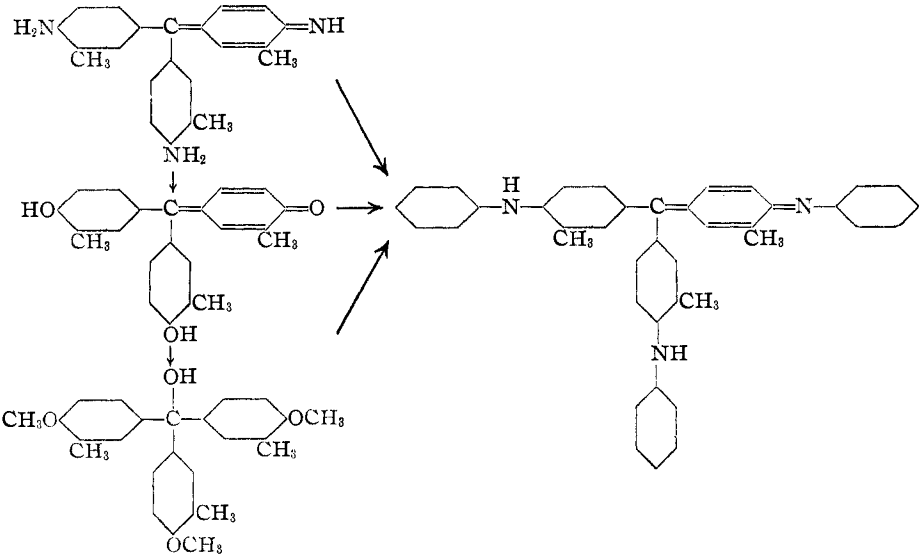
## The Constitution of *o*-Cresaurin, of Ros-*o*-toluidine, and of Triphenylros-*o*-toluidine

When *o*-cresol is substituted for phenol in the condensation reaction with carbon tetrachloride, the number of possible products is greatly augmented: first, as in the case of phenol, one or more of the cresol groups may attach itself to the central atom in such a manner that the product will have the hydroxyl group either *ortho* or *para* to the central carbon atom; and second, we might expect to find products in which the methyl group is *ortho* or *para* to the central carbon atom. We have proved, however, that what we call *o*-cresaurin has the constitution which we have assigned to it, and the following diagrammatic outline of our experimental work shows the reactions upon which we base the assertion. The two compounds marked with an asterisk have been previously described in the literature.

Having thus definitely proved the constitution of *o*-cresaurin, we showed that "New Fuchsin," or ros-*o*-toluidine, as we prefer to call it, gave rise to *o*-cresaurin and, therefore, must be the corresponding triamino compound, as Spiers surmised it to be.



It should be clearly understood, however, that commercial "New Fuchsin" is most likely a mixture of many materials. By making use of the basicity



of the tri-*p*-amino component (ros-*o*-toluidine) of this mixture, we have isolated it fairly pure.

The constitution of the blue dye, the phenylated ros-*o*-toluidine, which we have prepared, has also been determined. By comparing derivatives of the dye obtained by the action of aniline upon ros-*o*-toluidine with the corresponding derivatives of the dye obtained from either *o*-cresaurin or its trimethyl ether, we have shown that the formation of the blue dye depends upon the introduction of three phenylamino groups in place of the three amino, hydroxyl or methoxyl groups of the material with which we started.

There is, then, no essential difference in the behavior towards aniline between the reactions of the *o*-toluidine groups in ros-*o*-toluidine and the aniline groups of *p*-rosaniline. Lambrecht[7] claims that ros-*o*-toluidine cannot be phenylated, while Baines and Driver state that *o*-cresaurin does not react with aniline. Each claims that this non-reactivity is due to the presence of the methyl groups adjacent to the amino or hydroxyl group. Our evidence shows that, in order to phenylate the ring which contains the methyl group, it is only necessary to use a higher temperature than in the phenylation of the simpler one; consequently, when a compound which contains both aniline and *o*-toluidine groups is phenylated, the aniline groups probably will react first.

## Experimental Part

### The Condensation of *o*-Cresol with Carbon Tetrachloride in the Presence of Metallic Halides

*o*-Cresol may be condensed with carbon tetrachloride with the liberation of hydrogen chloride in the presence of zinc chloride, aluminum chloride or stannic chloride, both at atmospheric pressure and in an autoclave. When zinc chloride was used as the condensing agent, the procedure was that previously described for phenol, and when aluminum chloride was employed, it became necessary to have present an excess of *o*-cresol, since the latter is partially decomposed by aluminum chloride. With zinc chloride, the most favorable temperature seems to be about 125°; with aluminum chloride, near 100°; and stannic chloride apparently acts best when the condensation is carried out at 130° in an autoclave.

In all cases, the mechanism of the reaction is analogous to that which takes place when phenol is used, only the number of products which result is much greater. We have definitely isolated from the reaction mixture di-*o*-cresol carbonate, $3^1,3^2$-dimethyl-$4^1,4^2$-dihydroxybenzophenone, and *o*-cresaurin.

**$2^1,2^2$-Dimethyl-diphenyl Carbonate,** $(CH_3C_6H_4)_2CO_3$.—This carbonate is obtained in small amounts (4 to 5%) in the process of the condensation of *o*-cresol with carbon

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[7] Lambrecht, *Ber.*, **40**, 250 (1907).

tetrachloride in the presence of zinc chloride. It remains insoluble after the extraction of the reaction mixture with sodium hydroxide solution and can be obtained from the insoluble residue by extracting it with alcohol; m. p., 60°. It is identical with that previously described in the literature.[8]

**$3^1,3^2$-Dimethyl-$4^1,4^2$-dihydroxybenzophenone.**—This ketone together with *o*-cresaurin was removed from all other materials by treating the reaction mixture with steam in order to remove unchanged cresol and carbon tetrachloride and then treating the residue with dil. ammonium hydroxide. The insoluble matter was filtered from the ammonia solution of the ketone and dye, and these two substances were precipitated together by the neutralization of the ammonia solution with acetic acid. Since this ketone is soluble in ether and *o*-cresaurin is not, the mixture of the two, air-dried, was suspended in ether and allowed to stand for several hours. The insoluble dye was filtered off, the ether solution steam-distilled, and the residue redissolved in dil. ammonium hydroxide. Sulfur dioxide was passed into the ammonia solution, whereby the ketone was generally precipitated in crystalline form. Recrystallization from dil. ethyl alcohol gave a very light pink, crystalline product, the color of which changed to a light straw-yellow at 110°; m. p., 240°. The diacetyl derivative melts at 102°.

The ketone is soluble in alcohol, ether, acetone and acetic acid, and is insoluble in benzene, chloroform and petroleum ether.

Schroeter[9] fused together *o*-cresolbenzein and potassium hydroxide and from the product isolated what he thought was the ketone described above. We repeated this work and found that the product which melted near 138°, as given by Schroeter, was impure and after several recrystallizations melted near 160°. An analysis of the material led us to conclude that in the fusion, one of the two *o*-cresol groups was removed, rather than the one phenyl group. 3-Methyl-4-hydroxybenzophenone was prepared by the reaction between benzoyl chloride and *o*-cresol in the presence of anhydrous aluminum chloride. The ketone which was thus obtained melted at 163° and was identical with the material obtained from the fusion of *o*-cresolbenzein. The acetyl derivative of each melted at 68°, as did an intimate mixture of the two.

*Anal.* Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 79.0; H, 5.73.

It was evident from our method of purification that the low melting point of the material described by Schroeter was caused by the presence of some substance other than $3^1,3^2$-dimethyl-$4^1,4^2$-dihydroxybenzophenone, in admixture with the 3-methyl-4-hydroxybenzophenone.

**$3^1,3^2$-Dimethyl-$4^1,4^2$-dimethoxybenzophenone,** $(CH_3O—CH_3C_6H_3)_2CO$.—This ketone was prepared by two reactions: first, the methylation of $3^1,3^2$-dimethyl-$4^1,4^2$-dihydroxybenzophenone which had been obtained as a by-product in the condensation of *o*-cresol and carbon tetrachloride; and second, the action of 3-methyl-4-methoxyphenyl-1-magnesium bromide upon 3-methyl-4-methoxybenzaldehyde and subsequent oxidation of the hydrol thus obtained. This latter method established its constitution.

Five g. of $3^1,3^2$-dimethyl-$4^1,4^2$-dihydroxybenzophenone was dissolved in a solution of 3 g. of sodium hydroxide in 25 cc. of water. Ten g. of dimethyl sulfate was added and the mixture was refluxed for one hour. The dimethyl ether of the ketone crystallized from the hot solution and after the mixture had been allowed to cool, the crystals were washed with dil. sodium hydroxide solution and then recrystallized from petroleum ether; m. p., 116°.

3-Methyl-4-methoxyphenyl bromide was prepared by the action of dimethyl sulfate upon 4-bromo-*o*-cresol.[10] After crystallization from alcohol, it was obtained as colorless

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[8] Einhorn and Hollandt, *Ann.*, **301**, 115 (1898).

[9] Schroeter, *Ann.*, **257**, 74 (1890).

[10] Zincke and Hedenström, *Ann.*, **350**, 274 (1906).

plates, melting at 68°. Ten g. of the bromide was dissolved in absolute ether, 1.0 g. of very carefully dried magnesium powder was added and the mixture was gently refluxed until the magnesium had dissolved. To this solution was added 10 g. of 3-methyl-4-methoxybenzaldehyde.[11] The solution was boiled for 20 minutes and then steam-distilled until all volatile components had been removed. The brown, resinous material that remained was treated with ether, and the ether solution was then shaken with a dilute solution of potassium permanganate to which had been added a few drops of sulfuric acid. The ether solution was next washed successively with dil. sulfuric acid, dil. sodium hydroxide solution and water. After drying the ether with calcium chloride, petroleum ether was added to it and the solution evaporated to a small volume. On allowing this solution to cool, the dimethoxy-dimethyl-benzophenone crystallized; yield, 2.0 g.; m. p., 116°. An intimate mixture of this product with that obtained by the methylation of the ketone isolated from the condensation product of *o*-cresol with carbon tetrachloride gave the same melting point. As a further proof of the identity of the ketones which were prepared by the two methods that have just been described, we prepared, for comparison, the oxime of each. The identical oximes, m. p. 137°, were obtained.

## $3^1,3^2,3^3$-Trimethyl-$4^1,4^2$-dihydroxy-diphenyl-quinomethane, (*o*-Cresaurin) (I)

As mentioned above, *o*-cresaurin, together with the ketone, is extracted from the reaction mixture by dil. ammonium hydroxide, and is finally separated from the ketone through the insolubility of the dye in ether. In this manner it is obtained pure and is quite insoluble in water, alcohol, ether, benzene, petroleum ether, chloroform and bromobenzene; slightly soluble in acetone, hot nitrobenzene, acetic acid, ethylene chlorohydrin, anisole, amyl alcohol, *iso*propyl alcohol, butyl alcohol and methyl salicylate. *o*-Cresaurin was crystallized from acetic acid, methyl alcohol, ethyl alcohol, amyl alcohol, methyl salicylate, ethylene chlorohydrin and nitrobenzene, and gave in each case maroon-colored crystals which, once formed, became quite insoluble in the solvent from which they had been obtained. From the first four mentioned, it is obtained without solvent of crystallization.

This dye is very soluble in ammonium hydroxide and the hydroxides of the alkali and alkaline earth metals, the solution in each case having a dark wine color. With hydroxides of the heavy metals it forms lakes that are very insoluble. In dil. acid solutions *o*-cresaurin is quite insoluble, but it combines with the acids to form salts.

*Anal.* Calcd. for the fuchsone, $C_{22}H_{20}O_3$: C, 79.5; H, 6.03. Found: C, 79.0, 79.0; H, 6.08, 6.11.

## The Condensation of *o*-Cresol with Oxalic Acid in the Presence of Sulfuric Acid

*o*-Cresol (1 mole) and sulfuric acid (0.6 mole) were stirred for one hour at 100° to allow the formation of the 1-hydroxy-2-methylphenyl-4-sulfonic acid. Anhydrous oxalic acid (0.7 mole) was then added in small quantities during the next 48 hours. Continuous mechanical stirring aided the reaction in that it not only shortened the time necessary for completion but also prevented the viscous mass from becoming locally overheated. Without stirring, the mass foamed very badly after each addition of oxalic acid. The yield of pure dye isolated from the product varied from 39 to 42%.

*o*-Cresol, oxalic acid and sulfuric acid in the proportions indicated above were also mixed and heated in an autoclave but the yield was not improved. We attempted to

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[11] Gattermann, *Ber.*, **31**, 1150 (1898).

use phosphoric acid in place of sulfuric acid but the condensation was very slow and the yields were very poor.

## The Condensation of Potassium-*o*-cresolate and Carbon Tetrachloride

We repeated the reaction carried out by Baines and Driver, as closely as their meager description permitted. Potassium *o*-cresolate was prepared by evaporating a mixture of alcoholic solutions of equivalent amounts of potassium hydroxide and *o*-cresol. The two solutions were thoroughly stirred and then poured into a large U-tube that had previously been filled with pieces of pumice stone. The alcohol was evaporated and the potassium *o*-cresolate was dried by immersing the evacuated tube in an oil-bath, the temperature of which was maintained at 130°. A very slow stream of carbon tetrachloride vapor was passed through the tube for eight hours. A thermometer in each end of the U-tube showed that the inside temperature was always between 105 and 110°, the temperature used by Baines and Driver. At the end of the reaction the potassium salts were dissolved in water and the solution was filtered from the pumice stone. The filtrate was acidified with acetic acid and the precipitate separated into its components. When an autoclave was used, its tube was filled with pumice stone and the potassium *o*-cresolate was deposited and dried as before; carbon tetrachloride was added and the mixture was then heated at 150° for ten hours. The yield of pure *o*-cresaurin varied from 7 to 11%.

## Preparation of *o*-Cresaurin from Ros-*o*-toluidine

A mixture containing 50 g. of $3^1,3^2$-dimethyl-$4^1,4^2$-diamino-diphenylmethane, 150 g. of *o*-toluidine hydrochloride, 100 g. of *o*-toluidine, 10 g. of iron filings and 90 g. of *o*-nitrotoluene was heated to and maintained at 150° for two hours, the mixture being stirred continuously. Enough sodium hydroxide solution was then added to neutralize all of the hydrochloric acid present, and the excess of *o*-nitrotoluene and *o*-toluidine was removed by steam. The granular product remaining in the flask was air-dried and pulverized. This powder was sifted into 2 liters of dil. acetic acid (20 cc. of glacial acetic acid per liter) and the resulting suspension was stirred for one hour. The insoluble matter was filtered off and treated with more of the 2% acetic acid. The filtrate from this second extraction was added to the first filtrate and the clear solution was made slightly alkaline by the addition of dil. sodium hydroxide solution. The amorphous, purple precipitate formed was filtered off and air-dried; 52 g. of the carbinol was thus obtained.

A solution of 8.5 g. of sodium nitrite in 75 cc. of ice water was stirred vigorously while 10 g. of the carbinol dissolved in 50 cc. of concd. hydrochloric acid and 75 cc. of water was added. This mixture was stirred for 15 minutes and then heated to boiling for ten minutes. The black, amorphous material that precipitated was filtered off and digested with dil. ammonium hydroxide (1 to 15). After the insoluble material had been separated, the dark red, ammoniacal solution of the cresaurin was acidified by the addition of dil. acetic acid, and the precipitate was filtered off and air-dried. The yield of *o*-cresaurin as calculated from the $3^1,3^2$-dimethyl-$4^1,4^2$-diamino-diphenyl methane was 18%.

## Some Derivatives of *o*-Cresaurin

**$3^1,3^2,3^3$-Trimethyl-$4^1,4,^24^3$·triacetoxy-triphenylcarbinol, $[(CH_3)(CH_3COO)C_6H_3]_3$-COH.**—One g. of *o*-cresaurin, 1 g. of sodium acetate, and 20 cc. of acetic anhydride were refluxed together for 30 minutes. The hot solution was filtered and poured into cold water while the latter was vigorously stirred. The triacetyl compound separated as a light yellow oil that became crystalline upon standing. The crystals were filtered off and washed with dil. sodium hydroxide solution and water, and were then recrystallized from alcohol; m. p., 141°. The identical triacetyl compound resulted, whatever the source of *o*-cresaurin, whether from the condensation of *o*-cresol and carbon tetrachloride, *o*-cresol and oxalic acid, potassium *o*-cresolate and carbon tetrachloride, or from the diazotization of ros-*o*-toluidine.

*Anal.* Calcd. for $C_{28}H_{28}O_7$: C, 70.8; H, 5.90; Acetyl, 27.8. Found: C, 70.6; H, 5.88; Acetyl, 29.3.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-trihydroxy-triphenylmethane,** $[(CH_3)(HO)C_6H_3]_3CH$.—One g. of *o*-cresaurin, 1 g. of zinc dust and 20 cc. of acetic acid were stirred together vigorously and the mixture was heated to 80° for 15 minutes. The hot mixture was then filtered and the leuco base was precipitated by the careful addition of cold water. It was crystallized from benzene and petroleum ether; m. p., 200°. The identical leuco compound was yielded by *o*-cresaurin from each of the previously mentioned sources.

*Anal.* Calcd. for $C_{22}H_{22}O_3$: C, 79.2; H, 6.62. Found: C, 79.4, 79.6; H, 6.75, 6.87.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-triacetoxy-triphenylmethane,** $[(CH_3)(CH_3COO)C_6H_3]_3CH$.—The leuco compound was acetylated in the same manner as the dye. It was recrystallized from alcohol and then melted at 176°.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-trimethoxy-triphenylcarbinol,** $[(CH_3)(CH_3O)C_6H_3]_3COH$.—We prepared this carbinol by two different reactions: first, by methylating *o*-cresaurin, and second, by synthesizing it through the action of 3-methyl-4-methoxy-phenyl-1-magnesium bromide on $3^1,3^2$-dimethyl-$4^1,4^2$-dimethoxy-benzophenone.

The methylation of *o*-cresaurin is best carried out in the cold. The dye (1 mole) was suspended in an acetone solution of dimethyl sulfate (4 moles) and to this suspension was slowly added an aqueous solution of sodium hydroxide (4 moles). The alkali should be added so slowly that the reaction mixture is never more than slightly alkaline. After standing for 48 hours at room temperature the product was steam-distilled and the light yellow, granular material was digested with alcohol and then crystallized from methyl alcohol, ethyl alcohol, or petroleum ether. $3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-trimethoxy-triphenyl carbinol was thus obtained in colorless crystals; m. p., 157°.

Two g. of $3^1,3^2$-dimethyl-$4^1,4^2$-dimethoxy-benzophenone was dissolved in absolute ether, and the solution was added to an absolute ether solution containing 8 g. of 3-methyl-4-methoxy-phenyl-1-magnesium bromide. The mixture was warmed on the water-bath for 30 minutes, after which the reaction product was decomposed with ice and hydrochloric acid. The ether and other volatile components were then removed by steam, and the residue was dissolved in alcohol and the solution decolorized by means of animal charcoal. Upon diluting the filtered alcoholic solution, light yellow crystals were obtained and these, after recrystallization from benzene and petroleum ether, were found to be identical with the crystals obtained from the methylation of *o*-cresaurin.

*Anal.* Calcd. for $C_{25}H_{28}O_4$: C, 76.5; H, 7.15. Found: C, 76.3, 76.6; H, 7.22, 7.31.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-trimethoxy-triphenylmethyl Chloride,** $[(CH_3)(CH_3O)C_6H_3]_3CCl$.—Five g. of the trimethoxy-triphenylcarbinol was dissolved in 35 cc. of dry benzene, anhydrous calcium chloride was added, and dry hydrogen chloride was passed into the mixture until the precipitation of the red chloride-hydrochloride had ceased. A stream of dry air was then slowly passed through the benzene until the excess of hydrogen chloride had been removed and the colorless chloride had dissolved. The benzene solution was then filtered from the calcium chloride, concentrated, and to the cold solution were added 0.5 cc. of acetyl chloride, 15 cc. of absolute ether and 25 cc. of dry petroleum ether. After several hours, the $3^1,3^2,3^3$-trimethyl-$4^1,4^2,4^3$-trimethoxy-triphenyl-methyl chloride crystallized almost quantitatively in colorless, transparent crystals; m. p., 164°.

*Anal.* Calcd. for $C_{25}H_{27}O_3Cl$: Cl, 8.64. Found: 8.96, 8.99.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-trimethoxy-triphenylmethyl Peroxide,** $[(CH_3)(CH_3O)$-

$C_6H_3]_3C—O—O—C[C_6H_3(CH_3O)(CH_3)]_3$.—The free radical was prepared by the action of molecular silver upon a solution of the carbinol chloride. A known weight of the carbinol chloride and an equal weight of molecular silver were placed in a test-tube which was filled with dry bromobenzene and then quickly sealed. This tube was then shaken for a certain length of time. The solution of the free radical is dull red, but upon exposure to oxygen or air it is rapidly decolorized and a colorless peroxide is formed. In the formation of the peroxide, the theoretical amount of oxygen is absorbed.

The peroxide, insoluble in a mixture of ether and petroleum ether, is obtained in small, colorless crystals; m. p., 161–162°.

**$3^1,3^2,3^3$-Trimethyl-$4^1,4^2,4^3$-tribenzyloxy-triphenyl-carbinol,** $[(CH_3)(C_7H_7O)C_6H_3]_3$-COH.—Sixteen g. of *o*-cresaurin was dissolved in a solution of 8 g. of sodium hydroxide in 40 cc. of water and 40 cc. of acetone. Twenty-five g. of benzyl chloride was added and the mixture was then refluxed gently for eight hours. The reaction product was steam-distilled until free from all volatile components, and the light red, amorphous material that remained was crystallized from benzene and petroleum ether. The almost colorless crystals which were thus obtained were recrystallized from methyl alcohol; m. p., 182°.

**Bromine Derivatives of *o*-Cresaurin.**—*o*-Cresaurin (0.1 mole) was treated with bromine (0.4 mole) in glacial acetic acid. The amorphous product was dissolved in alkali and precipitated with dil. acetic acid. After the precipitate had been air-dried it was extracted with methylethyl ketone, and from the ketone extract we obtained a dibromo derivative. It crystallized from acetic acid as beautiful, maroon-colored needles.

*Anal.* Calcd. for $C_{22}H_{18}O_3Br_2$: Br, 32.6. Found: 32.4.

The tribromo compound that remained insoluble in methylethyl ketone was crystallized from ethylene chlorohydrin. This compound was recently described by Spiers.

**The Oxidation of *o*-Cresaurin.**—A very slow stream of air was washed with 5% sodium hydroxide solution and then passed through a solution of 5 g. of *o*-cresaurin in 5% aqueous sodium hydroxide. After several days the alkaline solution was acidified and the precipitate extracted with dil. ammonium hydroxide. From the ammoniacal extract 1.5 g. of pure $3^1,3^2$-dimethyl-$4^1,4^2$-dihydroxy-benzophenone was isolated; yield 41%. This oxidation was repeated but pure oxygen was used instead of air. The time necessary for nearly complete decomposition of the dye was shortened but the yield of ketone was not improved.

## Salts of *o*-Cresaurin with Mineral Acids

**The Hydrochloride,** $C_{22}H_{20}O_3.HCl$.—Dry hydrogen chloride was passed into a suspension of *o*-cresaurin in boiling acetic acid. In a very short time, the dye began to change from the amorphous form to a beautiful, light red, crystalline material with a golden luster. After recrystallization from acetic acid, the hydrochloride contained one molecule of solvent of crystallization, which was driven out by keeping the material at 80° for two hours under a pressure of 15 mm.

*o*-Cresaurin, when suspended in dilute aqueous hydrochloric acid, combines with part of the hydrogen chloride. Baines and Driver undoubtedly had a mixture of *o*-cresaurin and the hydrochloride when they crystallized the dye from 10% hydrochloric acid. It is probable, however, that this hydrogen chloride was removed when they dried their material at 150–160°.

**The Hydrobromide,** $C_{22}H_{20}O_3.HBr$.—Ten cc. of 40% hydrobromic acid was added to a boiling mixture of 3 g. of *o*-cresaurin in 40 cc. of acetic acid. A change of form, similar to that noted in the case of the hydrochloride, was also noted here. The light red crystals were recrystallized from acetic acid and then contained 1 molecule of solvent of crystallization which could be driven out as in the case of the hydrochloride.

**The Acid Sulfate,** $C_{22}H_{20}O_3.H_2SO_4$.—Two cc. of sulfuric acid was added to 5 g. of *o*-cresaurin which was suspended in 50 cc. of boiling acetic acid. The dye dissolved and the solution was then filtered and allowed to cool. The acid sulfate crystallized in glittering, light red crystals which contained 2 molecules of acetic acid that were easily removed under reduced pressure.

**The Normal Sulfate,** $(C_{22}H_{20}O_3)_2.H_2SO_4$.—Three g. of *o*-cresaurin was dissolved in 25 cc. of warm dimethyl sulfate and to this solution 1.5 cc. of sulfuric acid was added. The solution was then cooled and the normal sulfate was crystallized by the very careful addition of acetone and ether. It had the form of light orange-red crystals.

**The Perchlorate,** $C_{22}H_{20}O_3.HClO_4$.—Two cc. of 60% perchloric acid was added to a suspension of 3 g. of *o*-cresaurin in 25 cc. of boiling acetic acid. The dye immediately dissolved and the filtered solution was concentrated in a vacuum over soda lime. The perchlorate was obtained in light red crystals which contained 1 molecule of acetic acid of crystallization. This solvent of crystallization could be easily removed in a vacuum at 80–90°.

## $N^1,N^2,N^3$ - Triphenyl - $4^1,4^2,4^3$ - triamino - $3^1,3^2,3^3$ - trimethyl - triphenylcarbinol Chloride (Triphenyl-ros-*o*-toluidine) (III)

We have prepared triphenyl-ros-*o*-toluidine by starting with *o*-cresaurin, with the trimethyl ether of *o*-cresaurin, or with ros-*o*-toluidine. The condensations were carried out in the presence of sodium acetate, benzoic acid or stearic acid, and we found the last condensing agent to be the best. The yield of the blue dye varies considerably in the different reactions, the poorest yield being about 10%, obtained from the condensation of aniline with *o*-cresaurin in the presence of sodium acetate, and the best yield being about 90%, obtained from the condensation of aniline with the trimethyl ether of *o*-cresaurin in the presence of stearic acid.

From *o*-cresaurin, the procedure was as follows. A mixture of 3 g. of *o*-cresaurin, 3 g. of stearic acid and 40 g. of aniline was refluxed for 14 hours. The excess of aniline was removed from an alkaline solution by steam, the residue dissolved in ether, and the chloride of the dye precipitated by hydrogen chloride. This chloride was digested with hot benzene to remove the stearanilide with which it was mixed and was then recrystallized from methyl or ethyl alcohol.

From the trimethyl ether of *o*-cresaurin, the "blue" was prepared exactly as above except that the trimethyl ether, stearic acid and aniline were refluxed for only two or three hours. Benzoic acid could have been used instead of stearic acid.

When ros-*o*-toluidine was used in this synthesis, it was gently refluxed with aniline in the presence of benzoic acid or stearic acid as a catalyst; the latter proved to be the more efficacious. The separation of the triphenyl-ros-*o*-toluidine was accomplished as described above.

The dye, triphenyl-ros-*o*-toluidine, is quite soluble in nitrobenzene and chloroform, slightly soluble in alcohol and in acetic acid, and insoluble in practically all other usual organic reagents. It can be crystallized from either methyl or ethyl alcohol and is thus obtained as bronze-colored crystals. It is very insoluble in dil. inorganic acids and even in concd. hydrochloric acid, but dissolves in concd. sulfuric acid. From its salts, the carbinol is precipitated by dil. alkali in the form of a light, almost colorless mass. This carbinol is very soluble in ether and benzene, and from either of these solutions the chloride can be obtained by the addition of a little dry hydrogen chloride. The addition of some picric acid dissolved in benzene to the pink solution of the carbinol in benzene gives the very insoluble picrate. In an atmosphere of dry hydrogen chloride the solid imide chloride takes up a second and even a third molecule of the acid. These extra molecules of hydrogen chloride can be removed by heating the material in a vacuum at 80°, leaving the normal chloride.

*Anal.* Material crystallized from methyl alcohol. Calcd. for $C_{40}H_{36}N_3Cl$: Cl, 5.98. Found: 6.01.

**$N^1,N^2,N^3$ - Triphenyl - $4^1,4^2,4^3$ - triamino - $3^1,3^2,3^3$ - trimethyl - triphenylmethane,** $[(C_6H_5NH)(CH_3)C_6H_3]_3CH$.—This leuco base was prepared by the reduction of triphenyl-ros-*o*-toluidine with zinc dust in glacial acetic acid. The identical leuco base was obtained from samples of the dye prepared from *o*-cresaurin, the trimethyl-ether of *o*-cresaurin, and from ros-*o*-toluidine. In each case, it melted between 178° and 180° and the melting point of an intimate mixture of any two was also 178–180°. The base is oxidized to the dye by the addition of lead dioxide to a suspension of the colorless material in hydrochloric acid.

*Anal.* Calcd. for $C_{40}H_{37}N_3$: C, 86.0; H, 6.45; N, 7.52. Found: C, 85.9; H, 6.70; N, 7.54.

**α-Naphthyl- and β-Naphthyl-ros-*o*-toluidines.**—The trimethyl ether of *o*-cresaurin can be condensed with *p*-amino-biphenyl, α-naphthyl-, or β-naphthylamine in the presence of stearic acid, with the formation, in each case, of a blue dye. From the β-naphthyl compound a pure blue solution is obtained, from the α-naphthyl compound a purple-blue, and from the biphenyl compound a green-blue.

## The Use of *o*-Cresaurin as an Indicator

Buffer solutions of primary and secondary phosphate mixtures were prepared according to Sörensen's directions.[12] These solutions gave known hydrogen-ion concentrations ranging from *P*H 5.6 to *P*H 7.4 at intervals of about 0.2 Sörensen units. The hydrogen-ion concentration of each solution was determined by means of the hydrogen electrode, and after three drops of an acetone solution of *o*-cresaurin had been added the Sörensen value was again determined in order to be sure that the hydrogen-ion concentration remained the same. In this way, we found that *o*-cresaurin changes from the yellow color to a red color between *P*H 6.6 and *P*H 7.6. The end-point in the titration of a strong acid against a strong base can be very easily determined in the presence of *o*-cresaurin, as the color change from alkaline to acid is very apparent. The reverse change, from acid to alkali, is not very distinct because the dye tends to precipitate when added to the acid solution, and a slight excess of alkali is necessary before it redissolves.

This investigation was made with the assistance of the National Aniline and Chemical Company Fellowship. We wish to express our obligations for the generous aid we have thus received.

## Summary

1. A red dye, *o*-cresaurin, has been prepared by the condensation of *o*-cresol with carbon tetrachloride and by the condensation of *o*-cresol with

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[12] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1923**, 2d. ed., p. 114.

oxalic acid. Its constitution, which has hitherto been surmised, has now been definitely proved to be $3^1,3^2,3^3$-trimethylaurin.

2. "New Fuchsin," which is a mixture of several substances, contains, as has been surmised, $3^1,3^2,3^3$-trimethyl-*p*-rosaniline, or ros-*o*-toluidine. This dye has been isolated and, by converting it to *o*-cresaurin, its constitution has been established.

3. The blue dye, $N^1,N^2,N^3$-triphenyl-$3^1,3^2,3^3$-trimethyl-*p*-rosaniline, or triphenyl-ros-*o*-toluidine, has been prepared from *o*-cresaurin and from ros-*o*-toluidine, and its constitution has thus been proved. Other blue dyes have been prepared by condensing α-naphthylamine, β-naphthylamine, or *p*-aminobiphenyl with the trimethyl ether of *o*-cresaurin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

# A SIMPLIFIED METHOD FOR THE PREPARATION OF DIMETHYLGLYOXIME

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A great many processes for the manufacture of dimethylglyoxime have been evolved during the last half century.[1] Recent work on the preparation of oximes[2] brought facts to our attention which led us to undertake a study of the reactions to determine the optimum conditions both as to chemical yield and simplicity of manipulations.

The method now used for the manufacture of dimethylglyoxime consists in preparing first biacetyl monoxime from methylethyl ketone and an alkyl nitrite, and allowing an alkaline solution of this to react with hydroxylamine. In every case the yield of dimethylglyoxime is approximately 60%, whether based upon the methylethyl ketone or the hydroxylamine used.[3] This very significant fact can be explained by assuming a yield of approximately 60% of biacetyl monoxime in the first reaction and an almost quantitative yield of dimethylglyoxime in the second reaction. This explanation we have verified and note that by the usual method of procedure, much of the hydroxylamine used is in effect wasted.

We have attempted first to determine the most favorable conditions for the formation of biacetyl monoxime, and second to simplify its preparation, purification and utilization.

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[1] For bibliography see (a) Adams and Kamm, THIS JOURNAL, **40**, 1282 (1918); (b) *Univ. Illinois Bull.*, **16**, No. 43, 57 (1919).

[2] Semon and Damerell, THIS JOURNAL, **46**, 1290 (1924).

[3] (a) Gandarin, *J. prakt. Chem.*, [2] **77**, 414 (1908), 59 to 64% on methylethyl ketone, 70% on hydroxylamine hydrochloride. (b) Biltz, *Z. anal. Chem.*, **48**, 164 (1909), 56 to 62% on methylethyl ketone, 54 to 60% on hydroxylamine hydrochloride. (c) Adams and Kamm, Ref. 1 a, 50 to 55% on methylethyl ketone, 49 to 53% on hydroxylamine sulfate.