

### Summary

The preparation of a number of new substituted phenyldihaloarsines has been described.

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

## SALTS OF PHENOLPHTHALEIN

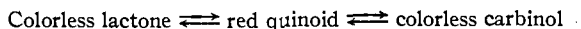
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The problem of constitution of the salts<sup>1</sup> of phenolphthalein has engaged the interest of many chemists since 1871, the date of discovery by Baeyer<sup>2</sup> of free phenolphthalein, which later he showed<sup>3</sup> possesses the lactone structure. The exact constitution of its salts, the reddening and fading effects produced by a variety of influences, and the correlations of chemical and color changes in solutions have been the chief problems giving rise to different opinions.

It is usually suggested that the color changes of phenolphthalein are in accordance with equilibrium of the following forms<sup>4</sup>



However, since the solid colorless mono-, di- and tri-basic salts all yield by dehydration corresponding red salts, it seems probable that more than one colored quinoid form and colorless carbinol forms are involved in equilibria both of the solid salts and in their solutions. Furthermore, no structures depict water of crystallization, which is always present in the colorless salts and in some of the red salts, and it seems certain that equilibria of such water molecules are involved in solutions, at least in saturated solutions, as well as in the dry salts. Then, too, it must be remembered, whereas isomerization, neutralization, hydrolysis, hydration and de-

<sup>1</sup> Only a few salts have hitherto been prepared, namely, salts of sodium, potassium, calcium and silver, and these possess different colors. The dry hydrated salts of sodium and potassium are colorless and their anhydrous salts are red. The silver salt is red. Red and green salts of calcium were described by Meyer and Posner, *Ber.* **44**, 1954 (1911). See experimental part of this paper.

<sup>2</sup> Baeyer, *Ber.*, **4**, 659 (1871).

<sup>3</sup> Baeyer, *Ann.*, **202**, 36 (1880).

<sup>4</sup> Apparently Berntsen was the first to use the quinoid formula in connection with phenolphthalein, *Chem.-Ztg.*, **16**, 1956 (1892). Also see Dehnst, *ibid.*, **17**, 654 (1893); Friedländer, *Ber.*, **26**, 172 (1893); Armstrong, *Proc. Roy. Soc. (London)*, 55 (1893). For opinions of the non-existence of the quinoid form for phenolphthalein, see Hjelt, *Chem.-Ztg.*, **18**, 3 (1894); Herzig and Meyer, *Ber.*, **29**, 138 (1896); Bistrzynski and Nencki, *ibid.*, **29**, 131 (1896); Schestakov and Nocken, *ibid.*, **47**, 331 (1914); Oddo, *ibid.*, **47**, 967 (1914); Consonno and Apostolo, *Gazz. chim. ital.*, **51**, [1] 50 (1921).

hydration are all probably involved, there are at least eight color-changing first causes.<sup>5</sup>

### Experimental

**Methods of Formation of Salts of Phenolphthalein.**—Owing to the great solubilities of salts of phenolphthalein in organic solvents, the insolubility of most inorganic bases and the capacity of phenolphthalein to form a series of salts with the same base, a variety of methods must be employed to obtain the different salts. The following methods were effective. (a) A metal, such as sodium, was dissolved in an alcohol, phenol, or ketone, and the resulting sodium compound was treated in the presence of the excess of the solvent, with the calculated quantity of phenolphthalein. On standing, the salt usually crystallized out. Promotion of formation of the red salts was influenced by the absence of water in the solvent. If the white hydrated salt was desired, usually a little water was added. The white salts were filtered off, washed with a little alcohol or methyl ethyl ketone, and dried in the desiccator. Whether or not an alkali alcoholate, etc., was first formed, the added water always was found to have formed the hydrated salts, free from combined alcohol, phenol or ketone.

(b) Solid hydrates were added to solutions of the phenolphthalein. These solids were gradually replaced by the solid salts. For the alkali metals, an organic solvent was used; for the alkali-earth metals, water was used. The latter salts could be formed very slowly in ordinary alcohol.

(c) The sodium or better the ammonium salt of phenolphthalein was treated with the acetate of the metal. When the heat of formation of the latter is less than that of the alkali acetate, the new salt of phenolphthalein can be formed.

(d) An ammoniacal solution of the base was treated with an ammoniacal or with an alcohol solution of phenolphthalein.

**Ammonium Salt.**—Anhydrous ammonia was passed into a mixture of methyl

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<sup>5</sup> COLORING. *By acids*, such as HCl, HClO<sub>4</sub>, etc., Meyer and Hantzsch, *Ber.*, **40**, 3482 (1907); Hofmann and Keimreuter, *ibid.*, **42**, 4856 (1909). *By alkalis*. Baeyer, *loc. cit.* *By water*. All colorless salts dissolve in water to give colored solutions. *By heat*. Herzig and Meyer, *Ber.*, **28**, 3258 (1895); **29**, 138 (1896); Green and Perkin, *J. Chem. Soc.*, **85**, 398 (1904). *By certain salts*, such as AlCl<sub>3</sub>, SnCl<sub>4</sub>, etc., Meyer and Hantzsch.<sup>4</sup> *By alcohol*, Meyer and Marx, *Ber.*, **40**, 3603 (1907). They prepared red alkali salts in absolute alcohol. *By pressure*. Oddo and Vassallo, *Gazz. chim. ital.*, **42**, 209 (1912). *By friction*. All white salts prepared in this paper were reddened by rubbing with a glass rod.

**BLANCHING.** *By acids*. Green and Perkin observed that neutralization by acetic acid of strongly alkaline solution in potassium hydroxide yielded unstable colorless C<sub>20</sub>H<sub>16</sub>O<sub>6</sub>K. *By more alkali*. Baeyer,<sup>2,3</sup> Menshutkin, *Ber.*, **16**, 315 (1883); Green and Perkin, above; Jones and Allen, *Am. Chem. J.*, **18**, 377 (1896); Hildebrand, *THIS JOURNAL*, **30**, 1914 (1908); Wegscheider, *Z. physik. Chem.*, **100**, 532 (1922). *By water*, McCoy, *Am. Chem. J.*, **31**, 520 (1904). *By cooling*. Meyer and Hantzsch, above. *By salts*, such as Na<sub>2</sub>CO<sub>3</sub>, Sztankay and Geyer, *J. Soc. Chem. Ind.*, **34**, 1167 (1915), German Patent 286,020. *By alcohol*. Draper and Draper, *Chem. News*, **55**, 133, 143 (1887); McCoy, *loc. cit.*; Schmatolla, *Ber.*, **35**, 1905 (1904); Jones and Allen, *Am. Chem. J.*, **18**, 377 (1896), explain the phenomena on the basis of suppression of the hydroxyl ions. Hildebrand, *THIS JOURNAL*, **30**, 1914 (1908), concludes that the alcohol unites with the phenolphthalein. Wegscheider, *Z. physik. Chem.*, **100**, 532 (1922), concurs in this opinion. Since red salts can be prepared in absolute alcohol and since colorless salts can be prepared in ordinary alcohol, it is evident that the concentration of water contained therein makes the difference.

ethyl ketone and phenolphthalein until the latter dissolved. On evaporating spontaneously in a desiccator over sulfuric acid, white crystals were obtained.

*Anal.* Calcd. for  $C_{20}H_{14}O_4 \cdot NH_4OH$ :  $NH_4OH$ , 9.51. Found (loss on heating to  $130^\circ$ ):  $NH_4OH$ , 9.92.

**White Monopotassium Phenolphthalein.**<sup>6</sup>—Prepared in methyl ethyl ketone from equivalent quantities of potassium hydroxide and phenolphthalein; glistening white rectangular plates and prisms, with truncated corners and beveled ends, were obtained.

*Anal.* Calcd. for  $C_{20}H_{14}O_4 \cdot KOH \cdot 2H_2O$ :  $H_2O$ , 13.17; K, 9.55. Found:  $H_2O$ , 13.12; K, 9.35.

This compound was also prepared from potassium cyanide. When its mixture with phenolphthalein in methyl ethyl ketone was permitted to stand for days, no precipitate formed. When a little water was added, an immediate voluminous precipitate of the above salt was obtained. Here either the cyanide was first added to phenolphthalein and the product was then hydrolyzed or the cyanide was first hydrolyzed and the potassium hydroxide then added.

**Red Monopotassium Phenolphthalein.**—A hot concentrated solution of equivalent quantities of potassium hydroxide and phenolphthalein in 95% alcohol was treated with a little ether and then was permitted to stand. After a few minutes there were formed rosetts of red needles and long rectangular leaflets which were blanched by ether and re-reddened by ordinary alcohol.

*Anal.* Calcd. for  $C_{20}H_{14}O_4 \cdot KOH \cdot H_2O$ : water, 9.18; K, 9.96. Found: water, 9.11; K, 10.01.

**Red Disodium Salts.**—The sodium hydroxide was prepared by Cornog's<sup>7</sup> or by Kuster's<sup>8</sup> method. For example, the necessary weight of sodium was dissolved in amyl alcohol and this mixture was treated with the calculated weight of phenolphthalein. On adding anhydrous ether to this deep red solution, little or no precipitate formed but the solution became indigo-violet by transmitted light. On adding water to this ether solution in quantities necessary for forming the hydrated salt, a voluminous red precipitate was obtained.

*Anal.* Calcd. for  $C_{20}H_{12}O_4N_2 \cdot 2H_2O$ :  $H_2O$ , 9.05; Na, 11.55. Found:  $H_2O$ , 9.76; Na, 11.30.

Contact with atmospheric moisture slowly changed this color through lighter reds to white.

**Red Calcium Salt.**—This was prepared by Meyer and Posner by quite an involved method. It is easily prepared by treating freshly ignited marble with phenolphthalein in the presence of a little water. Its composition was given as  $C_{20}H_{12}O_4Ca \cdot 2.5H_2O$ ; its more probable composition is  $C_{20}H_{14}O_5Ca \cdot 2H_2O$ , whose structural relations can be in-

<sup>6</sup> Kober and co-workers obtained the colorless monopotassium salt containing 1 mole of water and 1 mole of  $C_2H_5OH$ . When the sodium and the potassium salts were prepared by the author in the higher alcohols by their treatment with the metal, and proper equilibrium was established with the traces of water, the above salts free from alcohol of crystallization were always obtained.

Oddo and Vassallo<sup>6</sup> obtained the red monopotassium salt from (absolute) alcohol. Bassett and Halton claim to have disproved the formation of the red salt, because they obtained the white salt of Kober when they used (ordinary) alcohol. These apparent contradictions can be understood because the experiments of this paper point out the modifying influence of traces of water in various solvents.

<sup>7</sup> Cornog, *THIS JOURNAL*, **43**, 2573 (1921).

<sup>8</sup> Kuster, *Z. anal. Chem.*, **41**, 474 (1904).

dicated as  $\text{HO}(\text{CaCOOCC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{OH})=\text{C}_6\text{H}_4=\text{O}\cdot 2\text{H}_2\text{O}$ , and whose anhydrous salt, as  $\text{O}(\text{CaOCC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{OH})=\text{C}_6\text{H}_4=\text{O})_2$ .

The first formula involves the elimination of the phenol hydroxyl, an assumption which is disproved by the evolution of phenol itself at high temperatures. Furthermore, the analyses confirm the latter formulas:

Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Ca}\cdot 2\frac{1}{2}\text{H}_2\text{O}$	Ca, 9.98; 2.5H <sub>2</sub> O, 11.22
Calcd. for $2(\text{C}_{20}\text{H}_{14}\text{O}_5\text{Ca}\cdot 2\text{H}_2\text{O})$	Ca, 9.77; 5H <sub>2</sub> O, 10.98
Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Ca}$	Ca, 11.25
Calcd. for $\text{C}_{40}\text{H}_{26}\text{O}_9\text{Ca}_2$	Ca, 10.97
Found by M and P in the hydrated salt	Ca, 10.1; water, 11.3
Found by M and P in the anhydrous salt	Ca, 11.5; and 11.6
Found by the author in the hydrated salt	Ca, 9.61
Found by the author in the anhydrous salt	Ca, 10.74

**White Calcium Salt.**—Equivalent quantities of freshly ignited marble and phenolphthalein were placed in ordinary 95% alcohol. At first a very red solution and a red solid were formed. After shaking often during days and weeks, the red solution became pink and the red solid was replaced by a fluffy, white solid. By shaking and letting stand for a few seconds, the solution with suspended white solid could be decanted from the heavier red solid, filtered, washed with alcohol, dried and analyzed.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}_8\text{Ca}\cdot 2\text{H}_2\text{O}$ : H<sub>2</sub>O, 14.72. Found: H<sub>2</sub>O, 14.50. Calcd. for  $\text{C}_{40}\text{H}_{26}\text{O}_9\text{Ca}_2$  (see above): Ca, 10.97. Found: Ca, 10.96.

When dehydrated, this white salt became deep red at 110° and brown-black at 150°; both forms became bright red in moist air. Because the green anhydrous salt of Meyer and Posner becomes red on standing in the air and green again on heating, apparently the two anhydrous salts are two different compounds. However, when the green salt is pulverized in the absence of moisture, it becomes red, hence the green color is merely a fluorescent property of large red crystals.

**Piperidine Phenolphthalein.**—Upon mixing equivalent quantities of piperidine and phenolphthalein in methyl ethyl ketone or in alcohol, heating was observed; on cooling, white needles were obtained. After filtering and drying, they were found to give off slowly the odor of piperidine. On heating to 110° or higher, the material remained white.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{14}\text{O}_4\cdot \text{C}_8\text{H}_{11}\text{N}$ : loss in weight, 21.10. Found: 20.95.

Because this additive compound contains no carbinol hydroxyl, it gives no color on being heated. With water it yields a red solution because of preliminary hydration, followed by dehydration.

Formula	Method used	Color hydrated salt	Color anhydrous salt	Crystal form (hydrated)	Calcd. H <sub>2</sub> O	Found H <sub>2</sub> O	Calcd. M	Found M
2PP·Ba(OH) <sub>2</sub> ·4H <sub>2</sub> O	b	White (violet)	Red	Needles	10.24	10.66	15.61	15.30
2PP·S(OH) <sub>2</sub> ·4H <sub>2</sub> O	b	White (pink)	Red	Needles	10.85	11.48	10.55	10.24
2PP·Cu(OH) <sub>2</sub> ·3H <sub>2</sub> O	d	Grass-green	Brown-black	Needles	9.13	9.32	8.07	8.10
2PP·Co(OH) <sub>2</sub> ·3H <sub>2</sub> O	c	White (red)	Brown-black	Needles	9.20	9.48	7.53	7.74
2PP·Mn(OH) <sub>2</sub> ·3H <sub>2</sub> O	c	White (brown)	Black	Needles	9.25	9.66	7.05	7.39
2PP·Cd(OH) <sub>2</sub> ·3H <sub>2</sub> O	d	White	Red	Needles	8.61	8.91	13.43	13.65
2PP·Zn(OH) <sub>2</sub> ·3H <sub>2</sub> O	d	White	Scarlet	Needles	9.12	9.66	8.28	8.30

### Summary

1. A number of new salts of phenolphthalein have been prepared and studied. They are always additive compounds of phenolphthalein and the base. Usually two or more molecules of crystal water are also present.

2. It has been demonstrated that most hydrated salts are colorless and become colored by loss of water. Loss of water can be effected by heat, pressure, friction or certain solvents and such loss of water is probably a dehydration from the carbinol form to the quinoid form. The colors of dehydrated salts, containing either chromogenic or non-chromogenic metals, differ widely.

3. The probable cause of color of phenolphthalein salts is the quinoid chromophore. Hydration and dehydration are important influences effecting changes in color. Isomerization, neutralization, addition, hydrolysis and ionization attend phenolphthalein phenomena, but precede or are incidental to the transforming of colorless carbinol forms to the colored quinoid form.

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## THE PREPARATION AND PROPERTIES OF SOME SUBSTITUTED 2-METHYLTHIOPHENES

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In order to identify certain thiophene homologs in pyrolysis products, 2-methyl-5-ethylthiophene, 2-methyl-4-ethylthiophene and 2,3-dimethylthiophene were prepared for comparison. The preparation and properties of these compounds are reported here since these thiophene homologs were either unknown or imperfectly described.

2-Methyl-5-ethylthiophene was obtained in 40% yield by a modified Wolff reduction which consisted of heating the semicarbazide of 2-methyl-5-acetothienone with moist powdered potassium hydroxide. Steinkopf<sup>1</sup> has prepared this substituted thiophene in 10% yield by a Clemmensen reduction of 2-methyl-5-acetothienone, but he obtained insufficient material for determination of its physical properties.

The other two thiophene homologs were synthesized by the action of phosphorus sulfides on the proper substituted levulinic acids. While 2,3-dimethylthiophene has been prepared by Paal and Püschel<sup>2</sup> and by Grünewald,<sup>3</sup> it is noteworthy that our specimen had a boiling point about 3° higher than reported by them. This observation was checked on a purer

<sup>1</sup> W. Steinkopf, *Ann.*, **424**, 22 (1923).

<sup>2</sup> Paal and Püschel, *Ber.*, **20**, 2559 (1887).

<sup>3</sup> Grünewald, *ibid.*, **20**, 2586 (1887).