might cause confusion. The present investigation was initiated by such a set of circumstances. Table I includes some typical experiments we have performed attempting to produce the ester from sodium acetate in the presence of sodium chloride. The first product to crystallize was always impure *p*-bromophenacyl chloride.

Experimental[7]

Replacement Reactions.—Weighed quantities of the organic halide and the alkali halide were placed in a 25-ml. round-bottom flask and 30 ml. of 62% ethanol added. The resulting solution was refluxed for one and one-half hours, after which time it was allowed to cool. The crystals which formed were filtered, dried and weighed.

Anal.[8] Calcd. for C_8H_6BrClO: C, 41.15; H, 2.60. Found: C, 40.89; H, 2.62.

Synthesis of *p*-Bromophenacyl Chloride.—This compound was synthesized from bromobenzene, chloroacetyl chloride, and aluminum chloride by the method of Collet[4a] as modified by Judefind and Reid.[4b] We obtained white needles from aqueous alcohol, m. p. 117–118°, yield 80%.

Melting Point–Composition Curve.—Weighed quantities of the two compounds were mixed intimately. Since the mixtures gave melting ranges of 1.5–2°, the mean of the first and last values was used as the experimental points.

Solubility Determination.—Twenty-five ml. of the respective saturated halide solutions, properly thermostated, was removed and delivered into a weighed dish. The alcohol was evaporated at 45° and the weight of the residue determined.

Summary

1. *p*-Bromophenacyl chloride was shown to be formed from *p*-bromophenacyl bromide and sodium or potassium chloride in 62% ethanol.

2. The possibility of this replacement causing confusion when *p*-bromophenacyl bromide is used to identify acids in the presence of sodium chloride was shown.

3. The melting point–composition diagram and the solubility in aqueous ethanol of the two halides are given.

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(7) Melting points uncorrected.

(8) The microanalysis was performed by Dr. T. S. Ma, University of Chicago.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF EX-LAX, INC.]

The Permanent Fading of Alkaline Phenolphthalein Solutions

BY MAX H. HUBACHER

It is common knowledge that solutions of phenolphthalein in strong alkali are red when freshly prepared, but soon become colorless. This color fading is reversible, as the red color reappears when alkalinity is decreased.

Irreversible or permanent fading takes place when solutions of phenolphthalein in dilute alkali are exposed to the air for months. This permanent fading was observed by others and was attributed to the formation of a "tertiary carbinol-carbonate ion," but no experimental proof was submitted.[1]

It is known that alkaline phenolphthalein solutions are oxidized very slowly by atmospheric oxygen.[2] Now it has been found that irreversible fading is likewise due to air oxidation.

The following two compounds were isolated from faded phenolphthalein solutions: 2-(4′-hydroxybenzoyl)-benzoic acid (I) in a yield of 39–45% and a small quantity of phthalic acid. The remaining reaction product was a brown semi-solid mass on which further investigation is in progress, to isolate additional compounds. Up to the present time, no evidence has been revealed of the fate of the third benzene ring of the phenolphthalein molecule. It may be mentioned here that acid I can also be obtained from phenolphthalein in a yield of 80%, by hydrolysis of its oxime.[3]

Red phenolphthalein solutions sealed into Pyrex glass tubes retained their color for two years, at which time only pure phenolphthalein could be recovered.

In the colorimetric determination of phenolphthalein, these two types of fading should be taken into consideration, otherwise the results will be low.

Alkaline *o*-cresolphthalein solutions faded more slowly than phenolphthalein solutions and yielded 2-(3′-methyl-4′-hydroxybenzoyl)-benzoic acid (II) and a trace of phthalic acid. On the other hand, 3,4-dihydroxydiphenylphthalide fades rather rapidly and the compounds isolated from its faded solutions, in yields of 43%, were phenol and phthalic acid. This leads to the conclusion that not all phthaleins are air-oxidized to substituted *o*-benzoylbenzoic acids. The phenol obtained from the 3,4-dihydroxydiphenylphthalide must come from the unsubstituted benzene ring.

Eugenia H. Maechling[4] found that phenolphthalein can be oxidized in alkaline solution by hydrogen peroxide to phthalic acid. As a second reaction product, hydroquinone was isolated in this Laboratory. *o*-Cresolphthalein likewise yielded phthalic acid and toluhydroquinone. This is another example of the reaction first described by Dakin, who obtained catechol by hydrogen peroxide oxidation of salicylaldehyde and hydroquinone from *p*-hydroxyacetophenone.[5]

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(1) A. Thiel and G. Coch, *Z. anorg. allgem. Chem.*, **217**, 254 (1934).

(2) M. H. Hubacher, U. S. Patent 1,940,495 (*C. A.* **28**, 1366 (1934)).

(3) P. Friedlaender, *Ber.*, **26**, 176 (1893). He reports a m. p. of 210° dec. for the 2-(4′-hydroxybenzoyl)-benzoic acid.

(4) E. H. Maechling, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 586 (1938).

(5) H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909), and "Organic Syntheses," Coll. Vol. I, 141 (1941).

It is now possible to split the phenolphthalein molecule in three different ways. Two have just been outlined, namely, by air oxidation into 2-(4′-hydroxybenzoyl)-benzoic acid and by hydrogen peroxide into phthalic acid and hydroquinone. A third method is by fusion with potassium hydroxide, in which case benzoic acid and 4,4′-dihydroxybenzophenone are obtained.[6]

Experimental[7]

Fading of Alkaline Phenolphthalein Solution.—A solution of 127.2 g. (0.4 mole) of phenolphthalein in 16 liters of 0.2 *N* sodium hydroxide (3.2 moles) was kept at room temperature in an open bottle. Samples from this solution were taken occasionally. The absence of phenolphthalein was indicated when no precipitate formed after acidification. This was the case after five to eleven months, when the solution was brown in color. It was separated into two compounds, 2-(4′-hydroxybenzoyl)-benzoic (I) and phthalic acid, by fractional crystallization from acetic acid. Compound I (m. p. 208–210°), which separated first, was obtained in quantities of 39.5–45.0 g. (41–46%), and was purified for analysis by further recrystallization from acetic acid. It melted then at 211.1–212.9° with slight decomposition and showed no depression when mixed with an authentic sample of the acid.[3]

From 0.3 to 1.0 g. of phthalic acid (m. p. 195° with dec.) was obtained from the mother liquor.

Fading of Alkaline *o*-Cresolphthalein Solution.—A solution of 34.6 g. (0.1 mole) *o*-cresolphthalein (m. p. 224–225°) in 4 liters of 0.1 *N* sodium hydroxide solution was kept for one year in an open bottle, with no change in color. From this solution, 11.71 g. of *o*-cresolphthalein was recovered. From the acidic fraction, 2.53 g. of 2-(3′-methyl-4′-hydroxybenzoyl)-benzoic acid (II) (m. p. 223–224°) was obtained. A sample of II, purified further by crystallization from acetic acid, melted at 224.1–225.0°.[8]

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.10; H, 5.19.

The mother liquor also contained 0.21 g. of phthalic acid.

Fading of an Alkaline Solution of 3,4-Dihydroxydiphenylphthalide.—The original orange-colored solution of 31.8 g. (0.1 mole) of 3,4-dihydroxydiphenylphthalide[9] (m. p. 168.1–169.5°) in 4 liters of 0.1 *N* sodium hydroxide had become brown after standing for nineteen days at room temperature in an open Erlenmeyer flask and had a phenolic odor. This faded solution yielded 4.07 g. (43%) of phenol of b. p. 176–180° uncor. (the *p*-nitrobenzyl ether as well as a mixture with *p*-nitrobenzyl·phenyl ether melted at 90.1–90.3°) and 7.30 g. (44%) of phthalic acid.

Oxidation of Phenolphthalein with Hydrogen Peroxide.—56.0 grams of 30% hydrogen peroxide solution was added over a period of two hours to a stirred solution of 31.8 g. (0.1 mole) of phenolphthalein in 400 ml. of *N* sodium hydroxide. The temperature of the solution rose from 28 to 58° in the course of the reaction. Next day, the solution was treated to isolate the phenolic and acidic compound: 12.10 g. (55%) of hydroquinone[10] melting at 170.0–172.7° (the diacetyl derivative melted at 120.7–121.3°) and 14.24 g. (86%) of phthalic acid was obtained.

The same experiment was repeated, using an old sample of 30% hydrogen peroxide solution; 1.36 g. (6%) of hydroquinone and 10.89 g. (66%) of phthalic acid were isolated.

Oxidation of *o*-Cresolphthalein by Hydrogen Peroxide.—56.0 grams of 30% hydrogen peroxide solution was added in one portion to a solution of 33.6 g. of *o*-cresolphthalein (m. p. 224–225°) in 400 ml. of 0.1 *N* sodium hydroxide. The temperature of the reaction solution rose within a few minutes from 20 to 85°. The solution yielded 10.44 g. (43%) of toluhydroquinone[10] melting at 121.3–125.2° (no depression when mixed with an Eastman Kodak Co. sample melting at 125.8–126.3°) and 11.95 g. (74%) of phthalic acid.

Summary

Permanent or irreversible fading of alkaline phenolphthalein solutions was found to be caused by air oxidation. The products of this oxidation are 2-(4′-hydroxybenzoyl)-benzoic acid and phthalic acid. This fading was also noticed with *o*-cresolphthalein, which similarly yielded 2-(3′-methyl-4′-hydroxybenzoyl)-benzoic acid and phthalic acid, while 3,4-dihydroxydiphenylphthalide was oxidized to phenol and phthalic acid.

It was found that phenolphthalein and *o*-cresolphthalein on oxidation by hydrogen peroxide produced, besides phthalic acid, hydroquinone and *o*-toluhydroquinone, respectively. This reaction is another example of the reaction first described by Dakin.

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(6) A. Baeyer and J. B. Burkhardt, *Ann.* **202**, 127 (1880); F. F. Blicke and F. D. Smith, THIS JOURNAL, **51**, 1872 (1929).

(7) All melting points are corrected and were determined in a Hershberg precision melting point apparatus.

(8) Fr. Ullmann and W. Schmidt, *Ber.*, **52**, 2106 (1919), report a m. p. of 224–225° for their 2-(3′-methyl-4′-hydroxybenzoyl)-benzoic acid.

(9) Prepared according to Lin Che Kin, *Ann. Chim.*, **13**, 349 (1940), who reported a m. p. of 170–171° for the 3,4-dihydroxydiphenylphthalide; A. Baeyer (*Ann.*, **372**, 93 (1910)) observed a m. p. of 160–161°. Therefore the m. p. of 86° reported by S. Dutt (*Chem. Abst.*, **34**, 7886 (1940)) for the same compound appears incorrect.

(10) The hydroquinone, as well as the toluhydroquinone, were purified by sublimation at 110° and 10 microns in the apparatus described by M. H. Hubacher, *Ind. Eng. Chem., Anal. Ed.*, **15**, 448 (1943).