hours.[9] The yellow solid product was crystallized from about 10 milliliters of benzene, whereupon 0.17 g. of perylene, m. p. 270°, was obtained. The mother liquor was passed over a column of alumina–Super-Cel. The yellow band at the top of the column on elution gave 0.05 g. of additional perylene. The balance of the column on elution gave 1.0 g. of unchanged dinaphthyl. The *sym*-trinitrobenzene complex of perylene crystallized from benzene as brick red needles, m. p. 248.0–249.0°. *Anal.* Calcd. for $C_{23}H_{15}N_3O_6$: N, 9.03, Found: N, 8.83.

Anthanthrene.—One gram of 2,2′,7,7′-tetramethyl-1,1′-dinaphthyl was passed over palladium-charcoal[9] at 510° during one hour. A small amount of a solid orange-yellow material was collected as product which, after crystallization from toluene, separated as orange plates. A benzene solution of this crystalline material was passed over a short column of alumina–Super Cel. The yellow band formed at the top of the column was separated and eluted with benzene. The benzene solution was treated with *sym*-trinitrobenzene and deep red needles of a trinitrobenzene complex, m. p. 250–253°, separated. The trinitrobenzene complex was dissolved in acetic acid and tin and hydrochloric acid added to the solution. The mixture was heated for five minutes in order to reduce the trinitrobenzene portion of the complex. The warm mixture was decanted into ice water and the precipitated hydrocarbon filtered and dried. The precipitate was dissolved in benzene, and the solution treated with norite, filtered, and the filtrate concentrated. On cooling, there separated gold-yellow plates, m. p. 255–257° with decomposition.[10] *Anal.* Calcd. for $C_{22}H_{12}$: C, 95.62; H, 4.38. Found: C, 95.33; H, 4.84.

The catalyst used for the dehydrogenation was exhaustively extracted with benzene, but no material was extracted.

Summary

When 1,1′-dinaphthyl was treated with a palladium–charcoal catalyst at 490° it was converted to perylene.

When 2,2′-7,7′-tetramethyl-1,1′-dinaphthyl was treated with a palladium catalyst at 510° a small quantity of a compound whose properties were consistent with the structure of anthanthrene, was isolated, but most of the material was carbonized.

PITTSBURGH, PA. RECEIVED DECEMBER 29, 1945

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[9] For a description of the apparatus see *Ind. Eng. Chem., Anal. Ed.*, **17**, 673 (1945). For a description of the catalyst see THIS JOURNAL, **67**, 122 (1945).

[10] Scholl and Meyer, *Ber.*, **67**, 1229 (1934), give the melting point as 257°; Clar, *Ber.*, **72**, 1645 (1939), gives the melting point as 261°.

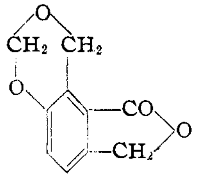
[CONTRIBUTION NO. 45 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Action of Formaldehyde on *m*-Hydroxybenzoic Acid. II

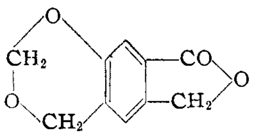
BY C. A. BUEHLER, JAMES O. HARRIS,[1] COMER SHACKLETT[2] AND BURTON P. BLOCK[3]

In the previous paper of this series[4] it was stated that two products are formed when formaldehyde reacts with *m*-hydroxybenzoic acid in hydrochloric acid solution. While the structure of the product melting at 254° was proved in the former paper, the structure of the other compound, melting at 176° when highly purified, is now to be considered. Having the formula $C_{10}H_8O_4$, the compound contains dioxanyl and phthalide rings since it gives, respectively, an orange to red precipitate when heated with phloroglucinol in strong sulfuric acid solution and a fluorescence develops with resorcinol and sulfuric acid.

Three structures are possible for the dioxanyl phthalide



I



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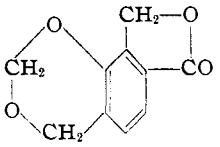
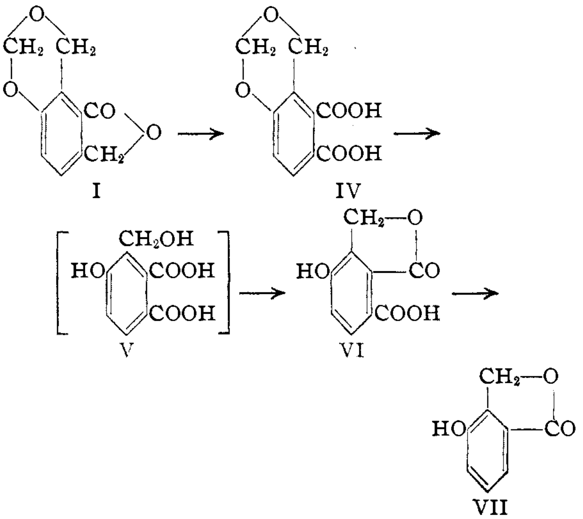


III

Oxidation with alkaline permanganate led to the formation of a product reconcilable only on the basis of formula I.



I IV V VI VII

The dicarboxylic acid, IV, which melts at 198°, could not be produced originally with certainty.

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[1] Present address: Monsanto Chemical Company, Anniston, Alabama.

[2] Present address: Clinton Engineer Works, Tennessee Eastman Corporation, Oak Ridge, Tennessee.

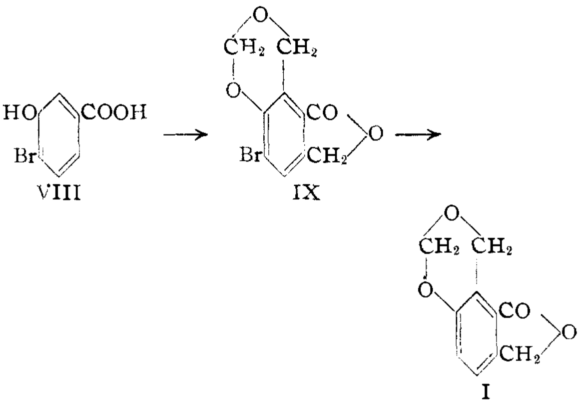
[3] Present address: Department of Chemistry, Purdue University, Lafayette, Indiana.

[4] Buehler, Powers and Michels, THIS JOURNAL, **66**, 417–418 (1944).

At times another product of the formula $C_9H_9O_5$, melting at 285–286° with effervescence, was recovered. The latter was at first thought to be a second oxidation product of I, but upon more thorough investigation it was found to be an acidic hydrolytic product of IV corresponding to formula VI. In fact, either IV or VI can be isolated from the oxidation mixture depending upon the amount of hydrochloric acid added previous to the recovery. That VI is 4-hydroxyphthalide-7-carboxylic acid was shown not only by the preparation of a series of derivatives, but by the fact that upon decarboxylation by heating in quinoline it gave 4-hydroxyphthalide, VII, m. p. 255–256.5°, identical with the first condensation product of *m*-hydroxybenzoic acid studied.[4]

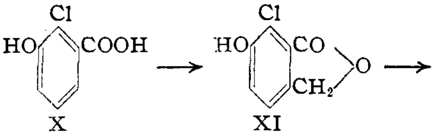
Although the evidence above supports formula I for the dioxanyl phthalide, other results, temporarily withheld for further study, point to formula II as being the correct one. In order to accumulate additional evidence bearing on the problem each of the phthalides in question was synthesized.

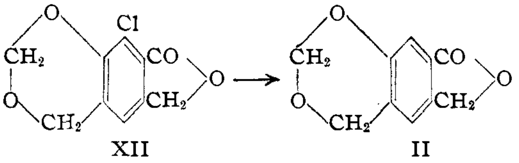
6-Hydroxymethyl-1,3-benzodioxan-5-carboxylic acid lactone, I, was produced as shown.


VIII IX I

The direct bromination of *m*-hydroxybenzoic acid gave 4-bromo-3-hydroxybenzoic acid, VIII, m. p. 225–226°. Upon condensation of the latter with formaldehyde in hydrochloric acid solution, the bromodioxanyl phthalide, IX, m. p. 196.5°, was formed. Debromination of an alcoholic solution of this compound by Busch's method[5] using hydrazine hydrate, aqueous potassium hydroxide and palladium–calcium carbonate catalyst produced the dioxanyl phthalide, I, m. p. 176.5–177°. A mixed melting point showed this product to be identical with the dioxanyl phthalide of m. p. 176° obtained directly from *m*-hydroxybenzoic acid.

6-Hydroxymethyl-1,3-benzodioxan-carboxylic acid lactone, II, was produced in a similar manner


X XI


XII II

The direct chlorination of *m*-hydroxybenzoic acid at low temperature gave 2-chlorobenzoic acid, X, m. p. 155–155.5°. The usual condensation with formaldehyde in hydrochloric acid solution produced the insoluble hydroxyphthalide, XI, m. p. 289.0–289.4° (290.3–290.7°, cor.). Further treatment of the latter with paraformaldehyde in sulfuric acid solution gave the chlorodioxanyl phthalide XII, m. p. 214.5–214.9° (216.2–216.6 cor.). Dechlorination of an alcoholic solution of this compound by a modification of Busch and Stove's method[6] using alcoholic potassium hydroxide, hydrogen at fifty pounds pressure and palladium–calcium carbonate catalyst yielded the dioxanyl phthalide, II, m. p. 164.5–165°, not identical with the original condensation product from *m*-hydroxybenzoic acid.

Experimental[7]

Preparation of Lactone of 6-Hydroxymethyl-1.3-benzodioxan-5-carboxylic acid (I).—*m*-Hydroxybenzoic acid, m. p. 199–200°, 50 g., was dissolved by stirring in 1 liter of 40% U. S. P. formaldehyde in a three-necked flask equipped with a mercury-sealed stirrer, a thermometer, and a glass tube with an opening of about 1 mm. in diameter leading to the bottom of the flask for introducing dry hydrogen chloride. Any excess of hydrogen chloride was removed through an exhaust tube, in the sidearm of the flask opposite to the one containing the inlet, attached to an aspirator pump. In about five minutes the acid had dissolved and then 1 liter of concentrated hydrochloric acid and 50 cc. of concentrated sulfuric acid were added, with stirring continued, and hydrogen chloride was passed rapidly through the entire solution heated to 60°. A white solid began to form after about one and one-half hours, but the reaction was continued for a total of three hours, at which time considerable more solid had separated. After cooling overnight in a refrigerator, the crystals were filtered off and washed until free from formaldehyde. One crystallization from methanol gave 21.5 g. of white crystals, m. p. 174–176°. Several crystallizations from a 1:1 methanol–water mixture elevated the melting point to 176°. The compound produces a fluorescence when treated with resorcinol and sulfuric acid in the usual manner, and it gives an orange to red precipitate when heated with a solution of phloroglucinol in concentrated sulfuric acid.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50, H, 4.20; neut. equiv., 192.2. Found: C, 62.32, 62.26; H, 4.19, 4.11; neut. equiv. (indirect), 183, 184.

1,3-Benzodioxan-5,6-dicarboxylic Acid (IV).—The lactone, 5 g., was dissolved in a solution of 10 g. of potassium hydroxide in 250 cc. of water by heating to 75–85°. A warm solution of 7.5 g. of potassium permanganate in 250 cc. of water was then added in small portions with stirring over a period of twenty minutes. All insoluble material was carefully filtered off and the yellow filtrate, after being made *slightly* acidic with hydrochloric acid, was evaporated to one-half its volume by warming, *not boiling*, on a hot plate (evaporation may be hastened if the solution is kept basic). Upon cooling in a refrigerator for at least an hour, 3.9 to 4.1 g. of yellow needles separated. By dis-

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[5] Busch, *Z. angew. Chem.*, **38**, 519 (1925).

[6] Busch and Stove, *Ber.*, **49**, 1063–1071 (1916).

[7] All melting points are uncorrected unless otherwise stated.

solving in the minimum amount of 5% sodium carbonate solution, boiling with decolorizing carbon, filtering, cooling and acidifying slightly with hydrochloric acid, 3 g. of white crystals, m. p. 198° with effervescence, were obtained.

Anal. Calcd. for $C_{10}H_8O_6$: C, 53.58; H, 3.60; neut. equiv., 112. Found: C, 53.72, 53.80; H, 3.72, 3.75; neut. equiv., 114, 111.

4-Hydroxyphthalide-7-carboxylic acid (VI).—The benzodioxan-dicarboxylic acid, 4 g., was boiled for ten minutes with 125 cc. of dilute hydrochloric acid (1:2). Solution occurred immediately, but about two minutes later a precipitate began to form and the odor of formaldehyde was apparent. After cooling in the refrigerator and filtering, 2.75 g. of light fluffy crystals, m. p. 273–274°, were obtained. Purification was accomplished either by crystallization from methanol or by dissolving in a minimum quantity of hot 5% sodium carbonate solution, boiling with decolorizing carbon, filtering and acidifying with concentrated hydrochloric acid. The melting point of the purest product is not sharp and it varies with the rate of heating. Some melting as high as 285–286° with effervescence was obtained, but ordinarily the value ran about 275° with effervescence.

Anal. Calcd. for $C_9H_6O_5$: C, 55.68; H, 3.12; neut. equiv., 97. Found: C, 55.76, 55.80; H, 3.42, 3.39; neut. equiv., 102, 104, 103.

The above acid may also be obtained directly from the benzodioxan-lactone: Seven grams oxidized as above was acidified with concentrated hydrochloric acid and then 25 cc. more was added. After evaporation to one-half volume by boiling, the solution on standing overnight in a refrigerator yielded 2.35 g. of crystals melting at 272° with effervescence. Purification by the sodium carbonate–hydrochloric acid treatment gave 1.6 g. which melted at 285–286° with effervescence.

Derivatives of 4-Hydroxyphthalide-7-carboxylic Acid.—(a) **4-Methoxyphthalide-7-carboxylic Acid Methyl Ester.**—The hydroxyphthalide carboxylic acid, 2 g., in a mixture of 200 cc. of absolute ethanol and 200 cc. of ether at 0° was treated in the usual manner with an ethereal solution of diazomethane. The residue obtained on evaporation was treated with 5% sodium bicarbonate solution at 60° to remove any excess of acetic acid, which had been used to destroy the excess of diazomethane, and then it was crystallized twice from a minimum amount of boiling methanol to yield 1.1 g., m. p. 166–168°.

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54; mol. wt., 222. Found: C, 59.66, 59.73; H, 4.50, 4.58; mol. wt. (cryoscopic, nitrobenzene), 224, 236.

(b) **4-Methoxyphthalide-7-carboxylic Acid.**—The ester of the methoxyphthalide carboxylic acid, 0.4 g., was refluxed in 20 cc. of 20% aqueous potassium hydroxide solution for two hours. Acidification of the cooled solution gave white needles which when crystallized three times from water weighed 0.3 g. and melted at 218–219°.

Anal. Calcd. for $C_{10}H_8O_5$: C, 57.69; H, 3.87; mol. wt., 208. Found: C, 57.42, 57.17; H, 4.03, 4.00; neut. equiv., 215, 211, 214.

(c) **4-Acetoxyphthalide-7-carboxylic Acid.**—4-Hydroxyphthalide-7-carboxylic acid, 2 g., and 2 g. of potassium carbonate were stirred into 10 cc. of acetic anhydride. After thirty minutes the reaction subsided and then 1 g. more of potassium carbonate and 5 cc. more of acetic anhydride were added. On standing twenty minutes, the mixture was diluted with 50 cc. of water and then acidified with hydrochloric acid, which caused a solid to separate. Crystallization twice from absolute ethanol by slow evaporation gave 2.3 g., m. p. 121–122°.

Anal. Calcd. for $C_{11}H_8O_6$: C, 55.98; H, 3.41. Found: C, 56.16, 56.48; H, 3.58, 3.75.

(d) **4-Acetoxyphthalide-7-carboxylic Acid Methyl Ester.**—4-Acetoxy-7-carboxyphthalide, 2 g., was methylated with diazomethane as before to give, upon crystallization twice from methanol, 1.6 g. of crystals, m. p. 111–112°.

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03. Found: C, 57.55, 57.35; H, 4.06, 4.17.

Saponification of this ester produced crystals, melting at 275–276°, which gave no depression in melting point when mixed with 4-hydroxyphthalide-7-carboxylic acid.

4-Hydroxyphthalide (VII).—4-Hydroxyphthalide-7-carboxylic acid, 3 g., in 20 cc. of quinoline was heated in a paraffin-bath at 175° for thirty minutes, at the end of which time the evolution of carbon dioxide ceased. The cooled solution was diluted with 50 cc. of water and upon acidifying with hydrochloric acid a solid separated. Some additional solid was obtained by extraction of the liquid remaining with ether. The combined solids were boiled with norite and about 150 cc. of water for several minutes, and the filtrate from this mixture on cooling yielded white needles. One crystallization from a methanol–water mixture (1:4) gave 1.5 g., m. p. 255–256.5°. The compound produces no appreciable depression in melting point when mixed with 4-hydroxyphthalide, m. p. 254°, obtained from *m*-hydroxybenzoic acid.

Anal. Calcd. for $C_8H_6O_3$: C, 64.00; H, 4.03; mol. wt., 150. Found: C, 64.12, 64.46; H, 4.18, 4.29; neut. equiv. (indirect), 151, 150.

Synthesis of 6-Hydroxymethyl-1,3-benzodioxan-5-carboxylic Acid Lactone (I)

4-Bromo-3-hydroxybenzoic Acid (VIII).—This acid was prepared by a modification of Berger's method[8]: To a clear solution of *m*-hydroxybenzoic acid, 18.2 g., in 180 cc. of glacial acetic acid, there was added, with stirring, a solution of 21.1 g. of bromine in 70 cc. of glacial acetic acid. Cooling under the tap was necessary to prevent a pronounced temperature rise during the first hour after the addition. Upon standing for twelve hours or more, the reaction mixture was distilled (the pressure produced by a good water pump was used at least until all excess bromine had distilled over) until 160 cc. of distillate came over. The residue was now cooled in a refrigerator to solidify the entire mass. Upon removal, the acetic acid soon began to melt and the mixture was stirred until the temperature rose to 14–15°. Filtration gave a solid which was washed with 100 to 200 cc. of cold water and dried overnight in a vacuum desiccator containing sodium hydroxide. Crystallization from a minimum amount of boiling water, using 2 g. of norite A, gave 5 g. of white crystals melting at 225–226° (Berger[8] gives 226.5–227.5°).

8-Bromo-6-hydroxymethyl-1,3-benzodioxan-5-carboxylic Acid Lactone (IX).—To a solution of 5 g. of 4-bromo-3-hydroxybenzoic acid in 150 cc. of 40% U. S. P. formaldehyde, 100 cc. of concentrated hydrochloric acid and 10 cc. of concentrated sulfuric acid were added. The solution in the condensation apparatus described above was heated to 60 ± 5° while dry hydrogen chloride gas was passed through with stirring. After four hours the reaction mixture, which now contained considerable solid material, was cooled in the refrigerator overnight. Filtration gave a solid which weighed 2.7 g. and which when crystallized from absolute ethanol melted at 196.5°. By concentrating the original filtrate to about one-third of its volume, 2.8 g. more of solid was recovered. This when crystallized from absolute ethanol twice also melted at 196.5°. The compound gives a blue-green fluorescence when treated with resorcinol and sulfuric acid and with phloroglucinol in concentrated sulfuric acid a bright orange precipitate forms.

Anal. Calcd. for $C_{10}H_7BrO_4$: Br, 29.48. Found: Br, 29.66, 29.56.

6-Hydroxymethyl-1,3-benzodioxan-5-carboxylic Acid Lactone (I).—The bromo-dioxanyl phthalide was debrominated by Busch's method.[5] One gram in 50 cc. of absolute ethanol was heated slightly with 10 cc. of aqueous potassium hydroxide solution to produce solution. Palladium–calcium carbonate catalyst, prepared by Busch and Stove's method,[6] 3 g., and 10 cc. of Eastman Kodak Co. practical hydrazine hydrate (42% aqueous solution) was added and the mixture was refluxed for thirty minutes. On cooling, the catalyst was filtered off and the residue was

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[8] Berger, *Rec. trav. chim.*, **40**, 628 (1921).

washed twice with hot alcohol. Acidification, evaporation down to 50 cc. and cooling gave a solid which, after crystallization from absolute ethanol, weighed 0.6 g. and melted at 176.5–177°. This product showed no appreciable depression when mixed with the 176° melting dioxanyl phthalide obtained directly from *m*-hydroxybenzoic acid. It gives positive tests for the dioxane and phthalide rings.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.80, 62.92; H, 4.51, 4.34.

Synthesis of 6-Hydroxymethyl-1,3-benzodioxan-7-carboxylic Acid Lactone (II)

2-Chloro-3-hydroxybenzoic Acid (X).—This acid was prepared essentially by Plazek's method[9] although we were unable to duplicate the excellent yield claimed: Dry chlorine, 10 g., was bubbled through a stirred solution of 20 g. of Eastman C. P. *m*-hydroxybenzoic acid in 100 cc. of absolute ethanol or methanol. About one hour was required for this operation, and the temperature was kept around −60° by immersion in a Dry Ice–acetone-bath. After removing the excess chlorine by passing air through the solution for fifteen minutes, 100 cc. of water was added, and the solution was evaporated down to 70 cc. Cooling overnight in a refrigerator gave white crystals which when washed with ice water and dried weighed 13.7 g. and melted at 145–152°. Solution in 50 cc. of boiling water, concentration to 20 cc. and cooling produced 11 g. of white crystals, m. p. 153–154°. Another crystallization from benzene elevated the m. p. to 155–155.5° (Mazzara[10] gives 156–157°).

(a) **2-Chloro-3-acetoxybenzoic Acid.**—The free acid, 5 g., was acetylated by a method similar to that used above for 4-hydroxyphthalide-7-carboxylic acid. One crystallization from water using decolorizing carbon gave 3.7 g. of a white solid melting at 147–149°. The compound was difficult to purify, but several crystallizations first from water and then from benzene brought the melting point to 152.5–153°.

Anal. Calcd. for $C_9H_7ClO_4$: Cl, 16.52, neut. equiv., 214.6. Found: Cl, 16.72, 16.71; neut. equiv., 214.

6-Hydroxy-7-chlorophthalide (XI).—2-Chloro-3-hydroxybenzoic acid, 5 g., in 75 cc. of 40% U. S. P. formaldehyde was treated with 75 cc. of hydrochloric acid and then anhydrous hydrogen chloride was bubbled through the solution at room temperature for thirty-five to forty minutes. The reaction mixture, containing some solid, was heated on the hot-plate for two to three hours. After thoroughly chilling, filtering, washing with water and drying, 4.7 g. of a white solid melting at 283–284° resulted. On crystallization from cellosolve (b. p. 133–137°), the melting point rose to 289.0–289.4° (290.3–290.7°, cor.) with some darkening about twenty degrees lower. This compound is alkali-soluble and gives a positive phthalide test and a negative dioxane test.

Anal. Calcd. for $C_8H_5ClO_3$: Cl, 19.21. Found: Cl, 19.02, 19.25.

(a) **6-Acetoxy-7-chlorophthalide.**—The hydroxyphthalide, 0.75 g., was acetylated by the method employed for 4-hydroxyphthalide-7-carboxylic acid, except that the reaction mixture was allowed to stand for twenty-four hours with occasional shaking. One crystallization from benzene gave 0.68 g. of a solid melting at 166–166.5°. Another crystallization from absolute ethanol elevated the melting point to 166.5–167°.

Anal. Calcd. for $C_{10}H_7ClO_4$: Cl, 15.65. Found: Cl, 15.43, 15.54.

(b) **6-Methoxy-7-chlorophthalide.**—The hydroxyphthalide, 1 g., was methylated as described previously[4] for 4-hydroxyphthalide, except that the reaction mixture was placed on a steam-plate for forty minutes and then it was allowed to stand overnight before acidification. One crystallization from benzene gave 0.6 g. of product softening at 175° and melting at 187°. Two more crystallizations from benzene yielded a solid softening at 185° and melting at 187–187.5°.

Anal. Calcd. for $C_9H_7ClO_3$: Cl, 17.85. Found: Cl, 17.69, 17.74.

8-Chloro-6-hydroxymethyl-1,3-benzodioxan-7-carboxylic Acid Lactone (XII).—The hydroxyphthalide, 3 g., in 40 cc. of concentrated sulfuric acid was treated with 3 g. of Eastman C. P. paraformaldehyde and the mixture was shaken until solution was complete. A straw-colored solution which darkened perceptibly on standing resulted. After about twenty-four hours, the solution was poured on cracked ice and the mixture was allowed to come to room temperature. Filtering, washing with water, and drying gave a solid which was crystallized first from benzene and then from absolute ethanol to yield 2.1 g. of a product melting at 212–213°. Several more crystallizations from absolute ethanol elevated the melting point to 214.5–214.9° (216.2–216.6° cor.).

Anal. Calcd. for $C_{10}H_7ClO_4$: Cl, 15.64. Found: Cl, 15.72, 15.80.

6-Hydroxymethyl-1,3-benzodioxan-7-carboxylic Acid Lactone (II).—The chlorodioxanyl phthalide was dechlorinated by Busch and Stove's method[6] with two modifications: (1) The palladium–calcium carbonate catalyst employed was two and one-half times richer in palladium and (2) it was necessary to dissolve the calcium carbonate support to insure a satisfactory recovery of the final product. The method follows: One gram of the chlorodioxanyl phthalide and 2 g.of the palladium–calcium carbonate catalyst in a freshly prepared solution of 2 g. of potassium hydroxide in 100 cc. of absolute ethanol were shaken for fourteen hours at room temperature in a Parr hydrogenator under a hydrogen pressure of fifty pounds. The catalyst with its support was filtered off and treated with hydrochloric acid until no more carbon dioxide was evolved. Sufficient water was added to dissolve the calcium chloride and the undissolved material was filtered off and taken up in 100 cc. of boiling absolute ethanol. After another filtration to remove the spent palladium, the solution was evaporated to dryness. Crystallization of the residue from water gave 0.73 g. of a white solid melting at 164–165° (nothing was recovered from the original alcohol filtrate). A second crystallization from water, using norite, yielded a white solid, m. p. 164.5–165°. This compound gives positive dioxane and phthalide tests and a negative chlorine test.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.45, 62.80; H, 4.71, 4.53.

Summary

A second product of the condensation of formaldehyde and *m*-hydroxybenzoic acid in acid medium is 6-hydroxymethyl-1,3-benzodioxan-5-carboxylic acid lactone.

The structure of this dioxanyl phthalide has been proved by the characterization of one of its oxidation products and through the synthesis of two suspected dioxanyl phthalides.

KNOXVILLE 16, TENNESSEE

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(9) Plazek, *Roczniki Chem.*, **10**, 770 (1930).

(10) Mazzara, *Gazz. chim. ital.*, **29**, I. 378–393 (1899).