Anal. Subs., 0.2367, 0.2634: CO_2, 0.2890, 0.3226; H_2O, 0.0406, 0.0457. Subs., 0.2649, 0.2892: N_2, 26.6, 28.6 cc. (23°, 731 mm.; 24°, 738 mm.). Calcd. for $C_{14}H_9O_{12}N_4As$: C, 33.6; H, 1.81; N, 11.2. Found: C, 33.3, 33.4; H, 1.92, 1.94; N, 11.13, 11.05.

Product Formed from the 2,8-Dimethoxydibenzo-arsenole Chloride in Alkaline Medium.—Five g. of 2,8-dimethoxydibenzo-arsenole chloride was heated with 20 cc. of 10% sodium hydroxide solution for six hours in a sealed tube at 150–160°. After opening the tube, the plastic residue was extracted thrice with hot water. It was then dissolved in pyridine and reprecipitated with water in order to purify it. This process was repeated four times. An amorphous substance was obtained, softening at about 85°.

The carbon and hydrogen content corresponded to Formula VIII. However, such a substance should have a very high melting point, thus it is not probable that the material described is really the oxide. This substance is exceedingly insoluble and could not be obtained in crystalline form.

Anal. Subs., 0.2111, 0.3024: CO_2, 0.4423, 0.6343; H_2O, 0.0822, 0.1186. Calcd. for $C_{28}H_{24}O_5As_2$: C, 56.94; H, 4.1. Found: C, 57.13, 57.20; H, 4.36, 4.39.

I wish to express my thanks and appreciation to the International Education Board in New York for the financial aid which made this work possible.

Summary

The following derivatives of dibenzo-arsenole have been prepared: (1) 2,8-dimethoxydibenzo-arsenole chloride, (2) 2,8-dimethoxydibenzo-arsenolic acid, (3) 1,3,7,9-tetranitro-2,8-dimethoxydibenzo-arsenolic acid.

They contain arsenic as a member of an unsaturated five-membered ring.

CHICAGO, ILLINOIS

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

POLYHYDROXY-ANTHRAQUINONES. VII. STRUCTURE AND SYNTHESIS OF HYDROXY-ANTHRARUFIN AND OF RUFIOPIN

BY S. V. PUNTAMBEKER[1] WITH ROGER ADAMS

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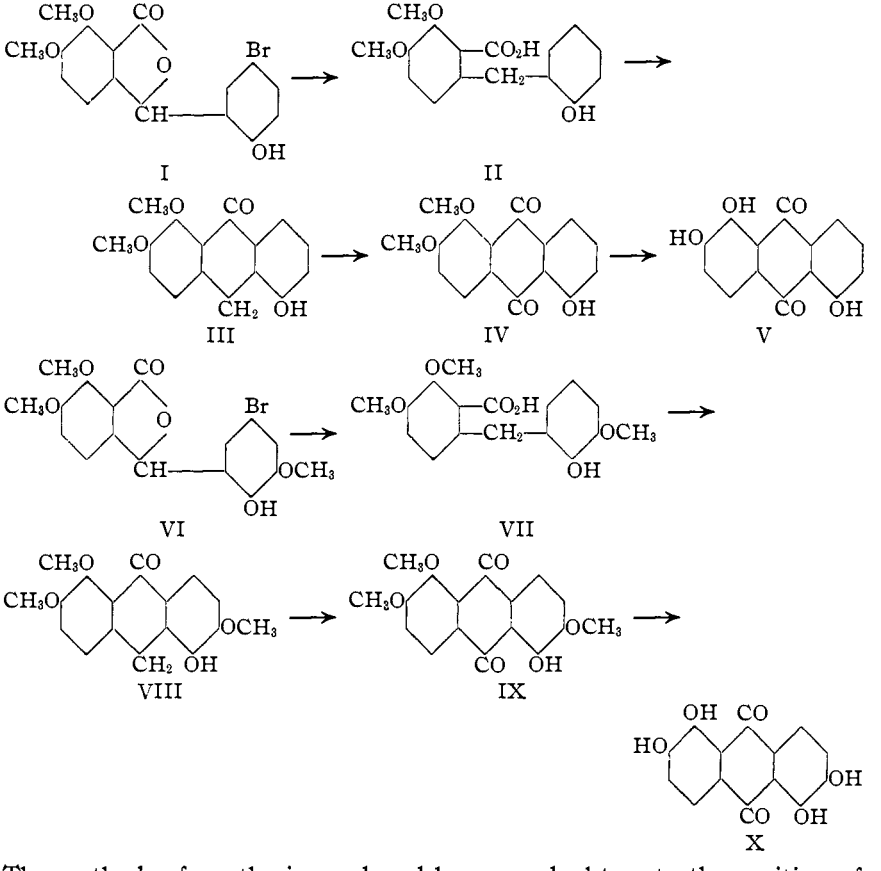
In recent papers[2] from this Laboratory, a method of condensing opianic acid with *p*-bromophenols to give phthalides was described in which the union has taken place in a position *ortho* to the hydroxyl. Upon reduction of these phthalides, benzylbenzoic acids were produced and at the same time the halogen was removed. These were dehydrated to anthrones, the latter oxidized to methylated anthraquinones, and then the anthraquinones demethylated. The method has now been applied to the syn-

[1] This communication is an abstract of a thesis submitted by S. V. Puntambeker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] (a) Jacobson with Adams, THIS JOURNAL, **46**, 2788 (1924). (b) Graves with Adams, *ibid.*, **45**, 2439 (1923). (c) Gardner with Adams, *ibid.*, **45**, 2455 (1923). (d) Jacobson with Adams, *ibid.*, **46**, 1312 (1924); (e) **47**, 283, 2011 (1925).

theses of 1,2,5-trihydroxy- and 1,2,5,6-tetrahydroxy-anthraquinones, by using *p*-bromophenol in the first and *p*-bromoguaiacol in the second case as shown in the following reactions.



The methods of synthesis employed leave no doubt as to the position of the hydroxyl groups and since the products proved to be identical with anthrarufin and rufiopin, respectively, the structures of these compounds have been definitely established.

Hydroxy-anthrarufin, because of its dyeing properties, has been synthesized by a number of methods; sulfonation of alizarin[3] in the presence of boric acid, and then hydrolysis; the action of sodium hydroxide upon anthrarufin;[4] the fusion of alizarin-disulfonic acid with sodium hydroxide and then elimination of a sulfonic group;[5] the action of sodium hydroxide

[3] Ger. pat. 156,960; *Chem. Centr.*, [I] **76**, 482 (1905).

[4] (a) Schunck and Römer, *Ber.*, **11**, 1179 (1878). (b) Liebermann and Boeck *Ber.*, **11**, 1617 (1878). (c) Graebe and Thode, *Ann.*, **349**, 215 (1906).

[5] (a) Ger. pat. 178,631; *Chem. Zentr.*, [I] **78**, 775 (1907). (b) Ger. pat. 210,863; *Chem. Zentr.*, [III] **80**, 243 (1909).

and sodium nitrate upon anthrarufin;[6] these methods do not, however, indicate with certainty the position of the three hydroxyl groups.

Rufiopin has been synthesized by Liebermann and Chojnacki[7] by heating opianic or hemipinic acid with concd. sulfuric acid. It has also been obtained by the fusion of hydroxy-anthrarufin sulfonic acid or the prolonged fusion of anthrarufin disulfonic acid with potassium hydroxide.[8] By the action of sulfuric acid upon protocatechuic acid,[9] or merely by heating protocatechuic acid alone,[10] rufiopin is obtained in small yields. In all of these methods more than one tetrahydroxyanthraquinone can, theoretically, be formed and consequently, the conclusion that the four hydroxyl groups are in the 1,2,5,6 positions has merely been a supposition. The synthesis of the 1,2,5,6-tetrahydroxy-anthraquinone and the identity of this substance with rufiopin positively identify the structure.

The color reactions and physical constants of these polyhydroxy-anthraquinones and their acetyl derivatives check with those for hydroxy-anthrarufin and rufiopin. Since the melting point of rufiopin has not been previously determined nor its acetyl derivative made, it was synthesized from protocatechuic acid in order to use it for comparison. The melting point was found to be 316–318° and that of the acetyl derivative 237–238°. The melting points of these two compounds agreed with the melting points found for the substance and its acetyl derivative synthesized as described above and the mixed melting points gave no depression.

Experimental Part

5,6-Dimethoxy-2-(2-hydroxy-5-bromophenyl)phthalide. (I).—This compound was prepared according to the directions of Jacobson and Adams,[2a] but the purification was carried out somewhat differently. The crude condensation product was extracted with ether to remove the *p*-bromophenol and the white residue crystallized once from glacial acetic acid, thus yielding a pure product; m. p., 218–219°; yield, 70%.

1,2-Dimethoxy-5-hydroxy-anthraquinone (IV).—A mixture of 5 g. of powdered 5,6-dimethoxy-2-(2-hydroxybenzyl)benzoic acid[2a] (II) and 5 g. of boric acid was treated with 15 cc. of C. P., concd. sulfuric acid and the mixture stirred vigorously for 15 minutes at room temperature. The resulting solution was allowed to stand for 15 minutes and then 15 g. of phosphorus pentoxide was added and the solution again vigorously stirred for three minutes. The solution warmed and changed in color from deep red to reddish-brown. On pouring it over ice the yellow anthrone (III) precipitated. It was filtered, washed and dried. The yield was 1.1 g. (17%). The anthrone (III) was not purified but was oxidized directly to the corresponding anthraquinone (IV).

[6] Ger. pat. 196,980; *Chem. Zentr.*, [II] **79**, 1505 (1908).

[7] Liebermann and Chojnacki, *Ann.*, **162**, 321 (1872).

[8] Ger. pat. 103,686; *Chem. Centr.*, [II] **70**, 640 (1899). Ger. pat. 103,988; *Chem. Centr.*, [II] **70**, 922 (1899).

[9] Noelting and Bourcart, *Bull. soc. chim.*, [2] **37**, 394 (1882).

[10] Kunz-Krause and Manicke, *Ber.*, **53**, 195 (1920).

To a solution of 2 g. of the crude 1,2-dimethoxy-5-hydroxy-9,10-dihydro-9-keto-anthracene in 20 cc. of glacial acetic acid was added a solution of 1 g. of chromium trioxide in 20 cc. of 50% acetic acid. Oxidation took place at once, the color of the solution changing from yellow to deep red. On diluting the acetic acid solution to 300 cc., a scarlet product separated. It was filtered, washed and dried, and found to be a chromium complex. By refluxing it for five hours with 25% hydrobromic acid, a mixture of dark material and the orange 1,2-dimethoxy-5-hydroxy-anthraquinone was obtained. A solution of 10% sodium carbonate completely dissolved the former, leaving the orange product, which was purified by crystallization from alcohol. It formed fine, orange needles; m. p., 230.5–231.5°; yield, 0.22 g., or 10%.

Anal. Subs., 0.1025: CO_2, 0.2544; H_2O, 0.0404. Calcd. for $C_{16}H_{12}O_5$: C, 67.60; H, 4.22. Found: C, 67.70; H, 4.41.

1,2,5-Trihydroxy-anthraquinone (**hydroxy-anthrarufin**) (V).—A solution of 0.15 g. of 1,2-dimethoxy-5-hydroxy-anthraquinone in a mixture of 17 cc. of glacial acetic acid and 8 cc. of constant-boiling hydrobromic acid was refluxed for 36 hours. On cooling the hot solution, the 1,2,5-trihydroxy-anthraquinone separated out in fine, long, brownish-red needles. They were recrystallized from glacial acetic acid; m. p., 273–274°; yield, 0.1 g., or 77%.

Anal. Subs., 0.072: CO_2, 0.1736; H_2O, 0.0225. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.12. Found: C, 65.78; H, 3.49.

1,2,5-Triacetoxy-anthraquinone.—A solution of 0.05 g. of 1,2,5-trihydroxy-anthraquinone in 20 cc. of acetic anhydride containing 0.5 g. of sodium acetate was refluxed for four hours. The resulting hot, yellow solution was filtered and the acetic anhydride was distilled under diminished pressure. The residue was extracted with water and then crystallized from alcohol. It formed small, yellow needles; m. p., 228–229°. From 0.1 g. of the anthraquinone 0.1 g. (67%) of the product was obtained.

Anal. Subs., 0.1100: CO_2, 0.2517; H_2O, 0.0375. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.42; H, 3.82.

5,6-Dimethoxy-2-(2-hydroxy-3-methoxy-5-bromophenyl)phthalide (VI).—To an intimate mixture of 15 g. of opianic acid and 15 g. of pure *p*-bromoguaiacol in a mortar, 39 cc. of 85% sulfuric acid was added slowly, with stirring. After the sirupy mass became homogeneous it was allowed to stand at room temperature for nine hours, at the end of which period it had completely solidified. Water was then added and the product crushed to a thin paste and filtered. After washing it free of the sulfuric acid, it was crystallized from 95% alcohol. It formed small, white needles; m. p., 163–164°. The yield of the pure phthalide was 20 g., or 70%.

Anal. Subs., 0.2840: 7.15 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{17}H_{15}O_6Br$: Br, 20.17. Found: 20.14.

5,6-Dimethoxy-2-(2-hydroxy-3-methoxybenzyl)benzoic Acid (VII).—A solution of 25 g. of 5,6-dimethoxy-2-(2-hydroxy-3-methoxy-5-bromophenyl)phthalide in 500 cc. of 10% sodium hydroxide was placed in a 2 liter, round-bottomed flask and treated with 80 g. of powdered zinc. The contents were heated just to the boiling point and mechanically stirred at this temperature for 14 hours. The excess of zinc was filtered and an excess of concd. hydrochloric acid added to the filtrate. The precipitate thus formed was a white, spongy solid. It was filtered, broken up and dissolved in cold, 10% sodium carbonate solution. The solution was filtered off from the undissolved matter and treated with an excess of concd. hydrochloric acid. This time a white, flocculent precipitate settled out. It was filtered, washed free of hydrochloric acid and crystallized from glacial acetic acid, forming white needles; m. p., 155–156°; yield, 14 g., or 71%.

Anal. Subs., 0.2186: CO_2, 0.5126; H_2O, 0.0970. Calcd. for $C_{17}H_{18}O_6$: C, 64.13; H, 5.70. Found: C, 63.97; H, 4.97.

5,6-Dimethoxy-2-(2-hydroxy-3-methoxy-5-bromobenzyl)benzoic Acid.—A cold solution of 1 g. of 5,6-dimethoxy-2-(2-hydroxy-3-methoxybenzyl)benzoic acid in 20 cc. of glacial acetic acid was treated gradually with 0.51 g. of bromine in 5 cc. of glacial acetic acid. The mass was cooled in an ice-bath and then taken out and allowed to come to the room temperature. A white product separated which was recrystallized from glacial acetic acid; m. p., 168–169°; yield, 0.8 g., or 65%.

Anal. Subs., 0.3000: 7.74 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{17}H_{17}O_6Br$: Br, 20.15. Found: 20.64.

1,2,6-Trimethoxy-5-hydroxy-anthraquinone (IX).—To a mixture of 5 g. of 5,6-dimethoxy-2-(2-hydroxy-3-methoxybenzyl)benzoic acid and 5 g. of boric acid, 20 cc. of 100% sulfuric acid was added during constant stirring. Immediately a dark red solution resulted, which warmed and changed to a deep blue color. At the end of 15 minutes it was poured over broken ice, and a dark brown product separated. It was filtered, washed with water and then with 10% sodium carbonate solution. A part dissolved, leaving behind a reddish-brown residue of anthrone; yield, 1.26 g., or 27%. The anthrone (VIII) was not purified but directly oxidized to the corresponding anthraquinone.

To a solution of 1.26 g. of crude 1,2-dimethoxy-5-hydroxy-9,10-dihydro-9-keto-anthracene in 20 cc. of glacial acetic acid was added a solution of 0.6 g. of chromium trioxide in 10 cc. of 50% acetic acid. The resulting solution was heated to 60° in the course of 15 minutes. This reaction mixture, in which a little dark orange product had separated, was poured into 200 cc. of water. The anthraquinone was filtered, washed and crystallized from glacial acetic acid, giving bright orange needles; m. p., 245–246°; yield, 0.76 g., or 58%.

Anal. Subs., 0.1151: CO_2, 0.2733; H_2O, 0.0483. Calcd. for $C_{17}H_{14}O_6$: C, 64.96; H, 4.46. Found: C, 64.78; H, 4.70.

1,2,5,6-Tetrahydroxy-anthraquinone (X).—A solution of 0.3 g. of 1,2,6-trimethoxy-5-hydroxy-anthraquinone in 35 cc. of glacial acetic acid and 15 cc. of constant-boiling hydrobromic acid was refluxed for 36 hours. Upon cooling the resulting dark red solution, the demethylated anthraquinone separated in red needles; yield, 0.18 g., or 72%. After crystallizing several times from glacial acetic acid, it melted at the constant temperature range 316–318°.

Anal. Subs., 0.1659: CO_2, 0.3755; H_2O, 0.0453. Calcd. for $C_{14}H_8O_6$: C, 61.75; H, 2.94. Found: C, 61.75; H, 3.05.

Rufiopin was made by heating protocatechuic acid[11] according to the directions of Kunz-Krause and Manicke[10] and was found to give an identical melting point and mixed melting point with the 1,2,5,6-tetrahydroxy-anthraquinone just described.

1,2,5,6-Tetra-acetoxy-anthraquinone.—A mixture of 0.27 g. of 1,2,5,6-tetrahydroxy-anthraquinone, 1 g. of freshly fused sodium acetate and 25 cc. of acetic anhydride was refluxed for four hours. The acetic anhydride was removed by distillation under diminished pressure, and water added. A yellow product separated out which was purified from glacial acetic acid; m. p., 237–238°; yield, 0.24 g., or 55%.

Anal. Subs., 0.1201: CO_2, 0.2647; H_2O, 0.0434. Calcd. for $C_{22}H_{16}O_{10}$: C, 60.00; H, 3.64. Found: C, 60.13; H, 4.04.

The acetylation of rufiopin produced the same tetra-acetoxy-anthraquinone as shown by melting point and mixed melting point.

[11] (a) Fittig and Mielch, *Ann.*, **152**, 40 (1869). (b) Fittig and Remsen, *Ann.*, **159**, 151 (1871).

Summary

Through syntheses from opianic acid, 1,2,5-trihydroxy-anthraquinone and 1,2,5,6-tetrahydroxy-anthraquinone have been produced. These proved to be identical, respectively, with hydroxy-anthrarufin and rufiopin, thus establishing with certainty the structures of these compounds.

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

A STUDY OF ALIPHATIC POLYSULFIDES[1]

BY D. TWISS

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The compounds that form the subject of this investigation are the sulfides of ethyl formate (I), ethyl thioformate (II) and ethyl dithioformate (III).

$S_x(CO.OC_2H_5)_2$ I $\quad$ $S_x(CS.OC_2H_5)_2$ II $\quad$ $S_x(CS.SC_2H_5)_2$ III

The object of this work is to study in these series of sulfides the influence that the increase of the number of sulfur atoms might have on the reactivity of the terminal groups and, further, to examine to what extent the stability of the sulfur atoms between the terminal groups might be influenced when the oxygen in the latter is replaced by sulfur.

Of each of these series the mono-, di-, tri- and tetrasulfide was prepared and the same reactions were applied quantitatively to each compound. In Series I and II, the mono- and disulfides had already been made; the members of Series III have not yet been described in the literature.

The starting materials for the preparation of these sulfides were those derivatives of potassium ethyl carbonate ($C_2H_5O.CO.OK$) in which the oxygen atoms were successively substituted by sulfur, as follows: (1) potassium O-ethyl thiocarbonate ($C_2H_5O.CO.SK$), known as Bender's salt;[2] potassium O-ethyl dithiocarbonate ($C_2H_5O.CS.SK$), known as potassium xanthogenate;[3] (3) potassium ethyl trithiocarbonate ($C_2H_5S.CS.SK$) prepared according to Chancel.[4]

Preparations

The monosulfide of ethyl dithioformate was prepared by the action of ethyl chlorodithiocarbonate on potassium ethyl trithiocarbonate in ether suspension: $C_2H_5S.CS.SK + Cl.CS.SC_2H_5 = S(CS.SC_2H_5)_2 + KCl$. The disulfide was obtained by the oxidation of potassium ethyl trithio-

[1] This publication is part of a thesis presented at the University of Geneva, Switzerland, in October, 1922.

[2] Bender, *Ann.*, **148**, 137 (1868).

[3] Zeise, *Berzelius' Jahres-Ber.*, **3**, 81 (1824).

[4] Chancel, *J. prakt. Chem.*, **53**, 176 (1851).