The author wishes to express her appreciation to Professor Treat B. Johnson and to Dr. Oskar Baudisch for their suggestions and criticisms during the progress of this work.

Summary

1. The mild conditions under which uric acid is oxidized are emphasized.

2. The extent of cleavage of uric acid by means of complex iron salts is shown.

3. No mechanism is suggested, but it is demonstrated that an intermediate compound must be formed because the very sensitive xanthydrol test is obtained only after the oxidation mixture has been heated on the water-bath.

4. Experiments show that the oxidation of uric acid by means of $[Fe(CN)_5H_2O]Na_3$ may be catalytic in nature, and brought about by means of auxiliary valences. The latter is proved by the formation of a brilliant red solution during oxidation.

New Haven, Connecticut

[Contribution from the Chemical Laboratory of Presidency College, Calcutta]

CONDENSATIONS OF ALDEHYDES WITH RESORCINOL AND SOME OTHER AROMATIC HYDROXY COMPOUNDS

By Rajendra Nath Sen and Nripendra Nath Sinha

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The condensation of aldehydes with various aromatic hydroxy compounds has been previously studied by several investigators.[1] A close study of these condensations brings out certain facts of great importance, as follows.

1. Though the modes in which these various condensations took place and the natures of the resulting products were different in many cases, yet in a few cases only two molecules of hydroxy compounds reacted with one molecule of the aldehyde, forming the pyrone ring with the elimination of water by the interaction of two hydroxyl groups in the *ortho* position to the reacting hydrogen atoms. The mode in which these condensations were carried out by the previous workers may be generally represented either as Type 1[1f] or Type 2[1e] (R is a phenyl residue).

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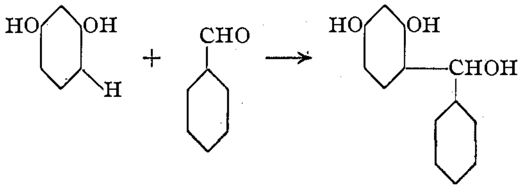
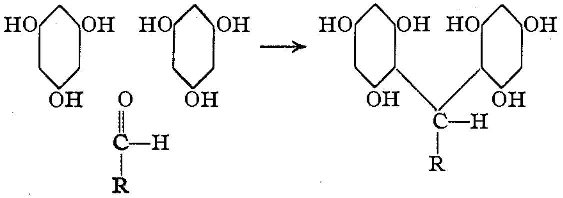
[1] (a) Michael, *Am. Chem. J.*, **5**, 339 (1883). (b) Causse, *Bull. soc. chim.*, [3] **3**, 861 (1890). (c) Hewitt and Pope, *Ber.*, **29**, 2824 (1896). (d) Michael, *J. prakt. Chem.*, **165**, 334 (1898). (e) Weidel and Wenzel, *Monatsh.*, **21**, 61 (1900). (f) Pope and Howard, *J. Chem. Soc.*, **78**, 1023 (1910). (g) Michael and Comey, *Am. Chem. J.*, **5**, 349 (1883). (h) Liebermann and Lindenbaum, *Ber.*, **37**, 2728 (1904). (i) Fischer and Jennings, *Ber.*, **27**, 1355 (1894). (j) Hofmann, *Ber.*, **26**, 1139 (1893). (k) Zenoni, *Gazz. chim. ital.*, **23**, II, 215 (1893). (e) Trzcinski, *Ber.*, **17**, 499 (1884). (m) Möhlau and Koch, *Ber.*, **27**, 2887 (1894).

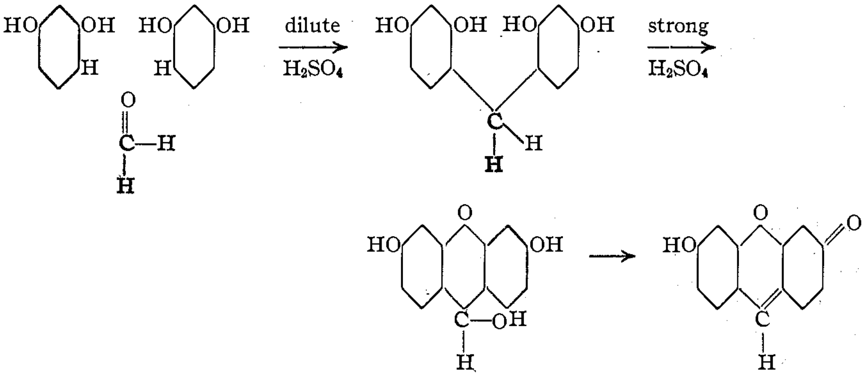


(1)



(2)

2. Even in those few cases where such pyrone-ring formation took place, the xanthenes were first isolated and then oxidized by different oxidizing agents to the corresponding fluorones. For instance, in Möhlau and Koch's work[1m] formaldehyde was first condensed with resorcinol by means of dil. sulfuric acid to form the xanthene; this xanthene was then isolated and in turn oxidized to fluorone by heating with concd. sulfuric acid, the reactions being represented thus,



3. The condensing agents used in the previous work were alcohol, sodium hydroxide, moderately concd. sulfuric acid, or alcoholic sulfuric acid, which could not bring about pyrone-ring formation and oxidation in one stage.

The present investigation has been taken up with two objects in view. The first is to study whether any such pyrone ring giving rise to xanthene can be formed and whether such leuco compounds can be oxidized to the corresponding fluorones in one stage by using the same condensing agent, thereby opening up new possibilities of the preparation of benzeins.

The second object has its origin in the fact that the majority of the compounds prepared during the course of this investigation are fluorescent, the fluorescence depending on the nature and position of certain groups.

It is therefore of considerable interest to study the influence of the number and position of hydroxyl and carboxyl groups on the existence and intensity of fluoresence, and also the influence of temperature and nature of the solvent.

Attention was first directed to find out a suitable condensing agent for bringing about the desired condensation as indicated before. With this object in view, sulfuric acid, d. 1.750, was first used as the condensing agent, but with this acid a product was obtained at 100° the alkaline solution of which was not fluorescent, which was insoluble in cold water and had no dyeing property, that is, it did not exhibit the characteristic properties of a benzein. Consequently, the temperature was raised to 200°, but at that high temperature only tarry product was obtained.

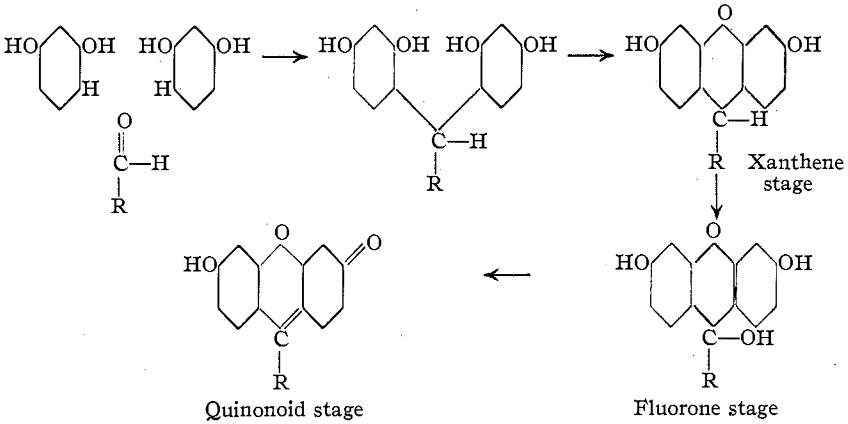
Next, acid of d. 1.840 was used and the condensation was effected by heating the reacting substances on the water-bath for about an hour; sulfur dioxide was evolved. It was found by testing the product that the desired result was obtained, that is, the product was insoluble in cold water, the alkaline solution was fluorescent and it possessed all the characteristic properties of a benzein.

Most of the compounds described in this paper have been obtained by condensing aldehydes with some aromatic hydroxy compounds by using the same condensing agent.

In order to study whether the reaction is of general application, different aldehydes have been used such as (1) chloral hydrate and paraldehyde from the aliphatic series, (2) benzaldehyde and substituted benzaldehydes from the aromatic series, (3) furfurole from the heterocyclic group and (4) phenetole-azo-benzaldehyde-sulfonic acid, which is a complex aldehydic compound with an azo group.

The mechanism of the reaction is explained as follows. The reaction takes place in several stages: (1) the two hydrogen atoms of the hydroxy compound in *ortho* position to one hydroxyl group and in *para* position to the other, interact with aldehydic oxygen; (2) then the two hydroxyl groups interact with the elimination of one molecule of water, giving rise to xanthenes; (3) these in turn are oxidized to fluorones at the expense of sulfuric acid, as is evident by the evolution of sulfur dioxide, the formation of which was indicated by development of a blue color on starch-iodide paper and the odor; (4) these oxidized products then assume the quinonoid structure by the elimination of another molecule of water. These various steps are indicated on the next page.

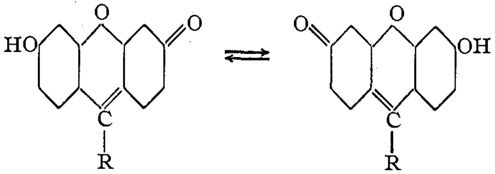
This constitution as given in the case of resorcinol-benzein is supported by the following facts: (1) analytical results show that its molecular formula is $C_{19}H_{12}O_3$; (2) analysis shows the formation of a monopotassium salt, and therefore indicates the presence of only one hydroxyl group; (3) analysis shows the formation of a monobenzoyl derivative, indicating thereby the presence of one hydroxyl group; (4) the physical properties, such as fluorescence, intensity of color, affinity for wool and silk, etc., are also in agreement with the suggested constitution.



Most of the compounds prepared during the course of this investigation dye wool and silk from an acid bath in yellow, orange or brown shades depending on the number, position and nature of the substituting groups, bromo compounds producing red and bluish-red shades. This may be illustrated by the following examples.

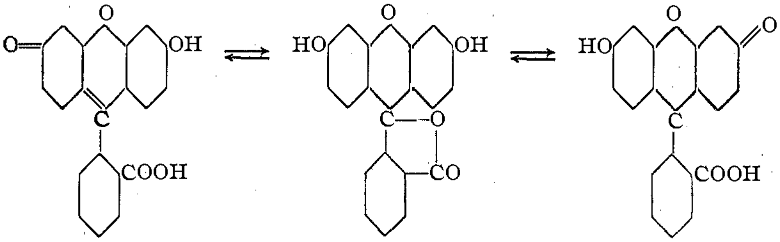
Dye	Shade of original compound	Shade of bromo compound	Remarks
1. Resorcinol-benzein	Yellow	Red	
2. Resorcinol-hydroxy-benzein	More orange than 1	Deeper than 1	Influence of one more OH group
3. Resorcinol-dihydroxy-benzein	More orange than 1	More bluish than 1	Influence of two OH groups
4. Resorcinol-phenetole-azo-benzein-sulfonic acid	Brown	More bluish than 1	Influence of additional azo group

These compounds resemble the fluoresceins in constitution and properties. Taking resorcinol-benzein as the typical compound of this series and fluorescein to be the typical compound of the fluoresceins, a comparison of their properties is of interest. Both compounds are precipitated from their solutions in sodium hydroxide as yellowish-red powders; both dissolve in alcohol with yellow-red color and green fluorescence, the intensity of which is greater in the case of fluorescein; both dissolve in sodium hydroxide giving dark red concd. solutions, but on dilution fluorescein gives an orange-green fluorescence and resorcinol-benzein gives a red-green fluorescence; both compounds can be brominated to tetrabromo compounds which dye wool and silk beautiful red shades. One very interesting fact about these compounds is that resorcinol-benzein is quinonoid in all its tautomeric forms,



Quinonoid Quinonoid

while fluorescein is not quinonoid in all its tautomeric forms.

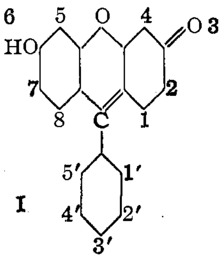


Quinonoid Non-quinonoid Quinonoid

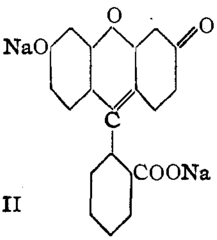
According to Watson's rule[2] a dye which is quinonoid in all its tautomeric forms should produce a deep shade (violet, blue or green). Resorcinol-benzein is, however, not of such a deep color, although it produces a deeper, more orange shade than fluorescein.

The second object of the present investigation is to study (1) the influence of the number and positions of hydroxyl and carboxyl groups, and (2) the influence of the temperature and the nature of the solvent on the existence and the intensity of fluorescence of these compounds.

Taking fluorescein to be the typical fluorescent substance, a comparison between this compound and other compounds with different groups in different positions is interesting.



I



II

Resorcinol-benzein (I) (or the sodium salt) which differs from fluorescein (II) by the absence of one carboxyl group in the phenyl residue in *ortho*

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[2] Watson, *J. Chem. Soc.*, **105**, 759 (1914).

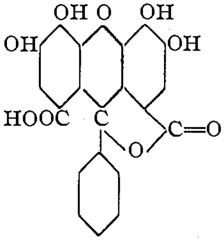
position to the central methane carbon atom is less fluorescent than fluorescein. That the intensity of fluorescence of these compounds is much less than that of the fluoresceins appears to be due to the fact that the intermediate phase is not strictly symmetrical.[3]

To study the effect of an hydroxyl group in *ortho* and *para* positions to the central methane carbon atom, resorcinol-*o*-hydroxybenzein and resorcinol-*p*-hydroxybenzein have been prepared. Both compounds are fluorescent in sodium hydroxide solution, the *ortho* compound showing a bluish fluorescence and the *para* compound exhibiting a greenish fluorescence of slightly greater intensity.

The effect of an additional methoxy group in the *meta* position to the central methane carbon atom is not very marked as shown by resorcinol-*p*-hydroxy-*m*-methoxybenzein, whereas resorcinol-*p*-methoxybenzein exhibiting bluish fluorescence shows the effect of a methoxy group in the *para* position, resorcinol-benzein as well as resorcinol-*p*-hydroxybenzein exhibiting green fluorescence.

Resorcinol-*m*-carboxy-*p*-hydroxybenzein, the condensation product of 5-aldehydo-salicylic acid and resorcinol, showed the influence of the carboxyl group in the *meta* position to the central methane carbon atom. This compound is feebly fluorescent. It has been shown that the presence of an hydroxyl group in the *para* position to the central carbon atom produces fluorescence. Now, as this compound, which contains one hydroxyl group in the *para* position and one carboxyl group in the *meta* position to the central carbon atom, is feebly fluorescent, it is logical to conclude that its feebly fluorescent character is due to the presence of the carboxyl group in the *meta* position. Here it is interesting to note the marked effect on fluorescence of a carboxyl group when in different positions in the phenyl residue.

β-Resorcylic-acid-benzein and gallic-acid-benzein show the influence of substituents in the benzene nuclei associated with pyrone oxygen. The former, having one carboxyl group in Position 2 and another in Position 7, is fluorescent while the latter, having one carboxyl group in Position 1 and another in Position 8, is not. Non-fluorescence of the latter in sodium hydroxide is due to (1) the presence of hydroxyl groups in the 4 and 5 positions and (2) the unsymmetrical intermediate phase,



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[3] Hewitt's Theory of Double Symmetrical Tautomerism, *Proc. Chem. Soc.*, **16**, 3 (1900).

One interesting fact about gallic-acid-benzein is that it is not fluorescent in alkaline solution, while its solution in concd. sulfuric acid is fluorescent. Instances of this type are already known; fluoran, for example, fluoresces in concd. sulfuric acid solution but not in alcoholic solution.

In pyrogallic-acid-benzein there are two hydroxyl groups in Positions 4 and 5, and also one in 6. This substance is not fluorescent. Its non-fluorescent character is most probably due to the presence of hydroxyl groups occupying positions *ortho* to pyrone oxygen, that is, the 4 and 5 positions. Such instances are also known in the case of fluorane derivatives.

Resorcinol-ethein, having a methyl group in place of the phenyl residue, is also fluorescent. Resorcinol-phenetole-azo-benzein-sulfonic acid is not fluorescent. This may be due to the presence of azo and sulfonic acid groups.

It is a curious fact that tetrabromo compounds of resorcinol-benzein, resorcinol-*o*-hydroxy-benzein, resorcinol-*p*-methoxy-benzein are non-fluorescent in sodium hydroxide, pyridine, and sulfuric acid solutions but are fluorescent in alcoholic solution, this fluorescence disappearing on dilution.

The effect of the influence of temperature on the intensity of fluorescence has been noted in a few cases. The fluorescence of certain substances, such as resorcinol-benzein, disappears at a higher temperature but reappears on cooling. This phenomenon has not yet received any satisfactory explanation. It may be due to the change of velocity of electrons and the consequent change in the period of vibration.

To study the influence of the nature of the solvent on the intensity and existence of fluorescence the following solvents were used: dil. aqueous sodium hydroxide, concd. sulfuric acid, redistilled ethyl alcohol, ether, glacial acetic acid, benzene, nitrobenzene, pyridine, acetone and in some cases methyl alcohol. From the observations recorded in the experimental part it may be concluded that the majority of compounds are fluorescent in sodium hydroxide and alcoholic solutions, and a few in pyridine and in sulfuric acid solutions. The majority of the substances, being insoluble in glacial acetic acid, benzene and ether, do not exhibit fluorescence in these liquids.

In consideration of the fact that the relation between chemical constitution and fluorescence has been very little investigated the results obtained during the course of this work have considerable theoretical interest.

Experimental Part

1. Resorcinol-benzein $C_{19}H_{12}O_3$ (I).—To a solution of 4.6 g. of dried resorcinol in 5 cc. of warm concd. sulfuric acid (d., 1.840) in a 300cc. conical flask fitted with an air condenser was added 2.2 cc. of dry benzaldehyde drop by drop and the mixture stirred constantly. Great heat was generated and an intense yellow color developed in the course of two or three minutes. When all of the benzaldehyde had been added, the flask with the contents was heated on the water-bath for about 45 minutes, when the odor of benzaldehyde was no longer perceptible. During the course of heating sulfur dioxide was evolved, as was evidenced by its odor and by the development of a blue color on starch-iodide paper.

When the mass became solid it was cooled, treated with ice-cold water, filtered and washed with cold water. The precipitate was dissolved in a solution of sodium hydroxide which was filtered and the original compound was reprecipitated with dil. hydrochloric acid, after which solution and precipitation were repeated. The product was finally crystallized from ethyl alcohol, when a microcrystalline yellow powder was obtained, and dried at 100°; yield, 3.8 g., or 74%. It is insoluble in cold water, ether, benzene, or glacial acetic acid, and is soluble in hot water (giving a yellow solution), in sodium hydroxide (a red solution), in concd. sulfuric acid (an orange solution), in acetone (a yellow solution), and in alcohol (a reddish-yellow solution). It imparts a red-green fluorescence to sodium hydroxide solution and pyridine solution, and an orange-green fluorescence to sulfuric acid and alcoholic solutions. Its solution in sodium hydroxide becomes colorless when heated with zinc dust, and again becomes colored by oxidation on exposure to air. It does not melt below 290°. On heating the substance on a nickel spatula over the flame it decomposes without melting. It dyes wool and silk a yellow shade.

Analyses. Subs., 0.1520, 0.1600: CO_2, 0.4402, 0.4640; H_2O, 0.0564, 0.0593. Calc. for $C_{19}H_{12}O_3$: C, 79.16; H, 4.16. Found: C, 78.98, 79.09; H, 4.12, 4.11.

POTASSIUM SALT.—Four g. of purified resorcinol-benzein was just neutralized with potassium hydroxide solution. The resulting salt solution was then filtered, the filtrate evaporated to a small bulk, and the neutral monopotassium salt was precipitated by alcohol. It was filtered off and finally crystallized from hot dil. alcohol as red crystals, which dissolve in water to give a red solution with red-green fluorescence.

Analysis. Subs., 0.1300: K_2SO_4, 0.0344. Calc. for $C_{19}H_{11}O_3K$: K, 11.99. Found: 11.8.

THE BENZOATE.—Five g. of pure resorcinol-benzein was benzoylated by the Schotten-Baumann process. There was thus obtained a light yellow powder which was purified by crystallization from alcohol. It melted at 141–142°.

Analyses. Subs., 0.1500, 0.1520: CO_2, 0.4373, 0.4430; H_2O, 0.0550, 0.0560. Calc. for $C_{26}H_{16}O_4$: C, 79.59; H, 4.08. Found: C, 79.44, 79.48; H, 4.07, 4.06.

2,3,5,7-TETRABROMO DERIVATIVE.—Five g. of the compound was brominated in alcohol by the slow addition of the calculated amount of liquid bromine. The product was crystallized from alcohol and was obtained as a red microcrystalline powder. It is soluble in sodium hydroxide solution (orange color, no fluorescence), in alcohol (orange color, feeble orange-green fluorescence), and insoluble in benzene or acetone. It dyes wool and silk a reddish-orange shade from an acid bath. It decomposes at about 200°.

Analysis. Subs., 0.1500: AgBr, 0.1866. Calc. for $C_{19}H_8O_3Br_4$: Br, 52.98. Found (Piria and Schiff's method): 52.93.

Resorcinol-benzein has been prepared previously by two other methods: (1) benzo-trichloride was condensed with resorcinol by heating the mixture on the paraffin-bath at 180° to 190° for five or six hours with zinc chloride; (2) benzoic acid was similarly condensed with resorcinol. The present method is simpler and more advantageous than the previous ones, as in this method less time and less energy (reaction temperature being the temperature of the water-bath) are required. The difficulty of the preparation of resorcinol-benzein by the earlier methods probably accounts for the fact that this substance did not gain so much importance as fluorescein.

2. Resorcinol-1′-hydroxybenzein.—A mixture of 4.6 g. of dried resorcinol, 2.4 cc. of salicylic aldehyde and 10 cc. of concd. sulfuric acid was heated on an oil-bath to 110° for 1$^1/_2$ hours. The product was then treated and purified in the same manner as described in the case of resorcinol-benzein. It is soluble in sodium hydroxide solution (orange color, red-blue fluorescence), in alcohol (yellowish-red color, no fluorescence), in acetone (yellow color, no fluorescence), in nitrobenzene (yellow color, no fluorescence) or in pyridine (deep red color, dull green fluorescence), and is insoluble in glacial acetic acid, benzene or ether. It does not melt below 260°. It dyes wool and silk a yellowish-orange shade from **an** acid bath.

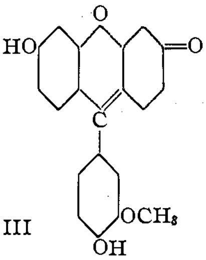
Analyses. Subs., 0.1450, 0.1420: CO_2, 0.3982, 0.3886; H_2O, 0.0508, 0.0508. Calc. for $C_{19}H_{12}O_4$: C, 75.00; H, 3.94. Found: C, 74.89, 74.63; H, 3.80, 3.98.

TETRABROMO DERIVATIVE.—Five g. of the substance was brominated by the slow addition of liquid bromine (1.5 cc.) to the alcoholic solution. The bromo compound was crystallized from alcohol and was obtained as red crystals; yield, 5.6 g. It is soluble in sodium hydroxide (red color, no fluorescence), in alcohol (orange-yellow color, feeble yellowish-green fluorescence), in concd. sulfuric acid (yellow solution, no fluorescence) or in pyridine (orange solution, no fluorescence). It decomposes at about 210° with change of color. It dyes wool and silk a red shade.

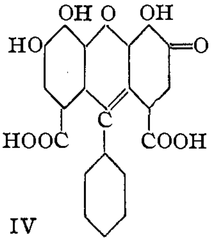
Analysis. Subs., 0.1512: AgBr, 0.1830. Calc. for $C_{19}H_8O_4Br_4$: Br, 51.58. Found: 51.52.

3. **Resorcinol-2′-methoxy-3′-hydroxybenzein** (III).—An intimate mixture of 6.6 g. of dried resorcinol with 4.6 g. of dried vanillin was added little by little to 10 cc. of concd. sulfuric acid (d., 1.840) in a conical flask with an air condenser, and the flask was heated on the oil-bath at 110–115° for about an hour. The subsequent process of purification was the same as in the case of the resorcinol-benzein. When crystallized from ethyl alcohol it formed a grayish-black, microcrystalline powder; yield, 5 g. It dissolves in sodium hydroxide solution (reddish-violet color, green fluorescence) and in concd. sulfuric acid (pink color, green fluorescence). It is insoluble in ether or benzene. It forms a bromo compound on treatment with liquid bromine, and dyes wool and silk from an acid bath with a yellowish-orange shade. It does not melt below 295°.

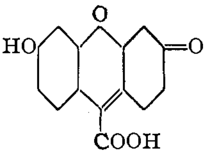
Analyses. Subs., 0.1600, 0.1301: CO_2, 0.4200, 0.3446; H_2O, 0.0599, 0.0487. Calc. for $C_{20}H_{14}O_5$: C, 71.80; H, 4.15. Found: C, 71.59; 71.74; H, 4.16, 4.17.



III



IV



V

4. **Gallic-acid-benzein** (IV).—Six and eight-tenths g. of well-dried gallic acid was condensed with 2.1 cc. of dried benzaldehyde in the same manner as in the case of the resorcinol-benzein, except that in this case the reacting substances were heated on an oil-bath to 120–125° for two hours. The substance was dissolved in sodium hydroxide and was reprecipitated by addition of dil. hydrochloric acid. It was then dissolved in 75% alcohol and the alcoholic solution was poured into hot water, when a precipitate was formed. The precipitate was again crystallized from hot alcohol, and a greenish microcrystalline powder was obtained; yield, 4 g. It dissolves in sodium hydroxide (deep red color, no fluorescence, and in concd. sulfuric acid (brownish-red color, red-green fluorescence). That the substance does not undergo any change in the sulfuric acid solution is proved by the fact that when the sulfuric acid solution is diluted with water the original substance is reprecipitated. It dissolves in acetone (yellowish-green color, no fluorescence), in alcohol (greenish color, no fluorescence), in pyridine (yellow color, no fluores-

cence), and in nitrobenzene (greenish solution); it is insoluble in glacial acetic acid in the cold but dissolves slightly when heated, and is insoluble in benzene and ether. It is a mordant dye, giving a brown shade in chrome-mordanted wool. It softens at 198°.

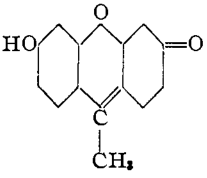
Analyses. Subs., 0.1300, 0.1640: CO_2, 0.2941, 0.3712; H_2O, 0.0345, 0.0439. Calc. for $C_{21}H_{12}O_9$: C, 61.76; H, 2.94. Found: C, 61.69, 61.73; H, 2.95, 2.97.

5. Condensation of Chloral Hydrate and Resorcinol (V).—To the solution of dried resorcinol in sulfuric acid was added 4.95 g. of dried chloral hydrate. The first action of sulfuric acid was to liberate the aldehyde chloral which acts on resorcinol. The reaction mixture was heated on the water-bath, when there was much frothing and copious fumes of hydrogen chloride (detected by the formation of ammonium chloride) and sulfur dioxide (detected by starch-iodide paper) escaped. The heating was continued for four to five hours. The cold mass was treated with ice-cold water. As the substance is soluble in cold water, the least quantity of water, containing a little hydrochloric acid, was used in washing. The same method of purification was adopted as in the case of the first compound; yield, 2 g. It dissolves in sodium hydroxide solution (red color, red-green fluorescence) and in sulfuric acid (yellow color, no fluorescence). One peculiarity of this substance is that the red color of the alkaline solution changes to orange on dilution. It is insoluble in glacial acetic acid, benzene, ether or acetone. The substance did not give any test for halogen. It dissolves in sodium carbonate solution with evolution of carbon dioxide. It dyes wool and silk a very light yellow. It does not melt below 295°.

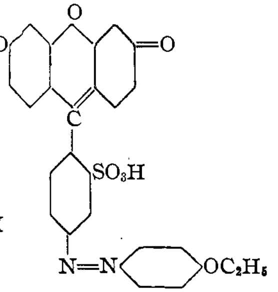
Analyses. Subs., 0.1400, 0.1200: CO_2, 0.3362, 0.2877; H_2O, 0.0390, 0.0335. Calc. for $C_{14}H_8O_6$: C, 65.62; H, 3.12. Found: C, 65.49, 65.38; H, 3.09, 3.10.

6. Resorcinol-ethein (VI).—Four and four-tenths g. of dried resorcinol was condensed with 1.76 cc. of paraldehyde in the usual manner. Ice-cold water was poured into the solid mass, the precipitate thus formed was dissolved in sodium hydroxide solution, the compound reprecipitated by dil. hydrochloric acid, the solution filtered, and the substance dried, washed with benzene and finally crystallized from 75% alcohol. It was obtained as a black, microcrystalline powder. It does not melt or decompose below 290°. It dissolves in sodium hydroxide solution (red color, red-green fluorescence, the intensity of which is almost equal to that of resorcinol-benzein). It is soluble in alcohol (orange color) and is insoluble in ether, benzene or nitrobenzene. It dyes wool and silk a yellowish-orange shade.

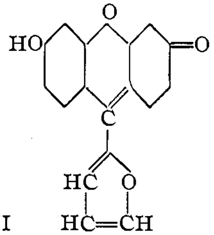
Analyses. Subs., 0.1200, 0.1350: CO_2, 0.3264, 0.3665; H_2O, 0.0476, 0.0534. Calc. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.40. Found: C, 74.18, 74.04; H, 4.40, 4.39.



VI



VII



VIII

7. Resorcinol-phenetole-azo-benzein-sulfonic Acid (VII).—A thorough mixture of 6.8 g. of recrystallized azo-aldehyde[4] with 4.4 g. of resorcinol in a mortar was added, little

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[4] Green and Sen, *J. Chem. Soc.*, **97**, 2243 (1910).

by little, to 10 cc. of sulfuric acid. A deep red color developed and great heat was generated. The mixture was thoroughly stirred and heated on an oil-bath at 130–140° for three hours. Sulfur dioxide was evolved. The solid mass was treated with ice-cold water. A portion was tested to prove the absence of azo-aldehyde, by means of phenylhydrazine acetate. The usual method of purification was followed; yield, 3 g. It dissolves in sodium hydroxide solution (brown color), in alcohol (brownish-yellow color) and in sulfuric acid (brown-red color). It is insoluble in nitrobenzene or ether. It does not fluoresce in any of the solvents, perhaps owing to the presence of sulfonic acid and azo groups. It dyes wool and silk from an acid bath a brownish-yellow shade.

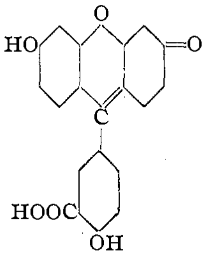
Analyses. Subs., 0.1679: 8.5 cc. of N_2 (30°, 760 mm.). Calc. for $C_{27}H_{20}O_7N_2S$: N, 5.5; S, 6.20. Found: N, 5.50; S, 6.00.

8. **Resorcinol-furfurein** (VIII).—To a solution of 6.6 g. of resorcinol in 10 cc. of sulfuric acid in a flask surrounded by freezing mixture was added 2.6 cc. of furfurole drop by drop while the mixture was constantly stirred. The substance assumed first a blue, then a reddish-violet and finally a blue-black color. After all of the furfurole had been added the flask was heated on the water-bath for half an hour, when sulfur dioxide was evolved. The substance is highly soluble in water. Therefore sulfuric acid was removed as barium sulfate by the addition of barium carbonate. The solution was filtered, the filtrate was evaporated to a small bulk and concd. hydrochloric acid was added. The solution was filtered and the precipitate was collected and finally crystallized from alcohol; yield, 3 g. It is soluble in sodium hydroxide solution (red color, red-green fluorescence), in concd. sulfuric acid (reddish-yellow color) and is insoluble in benzene or ether. It does not melt below 280°.

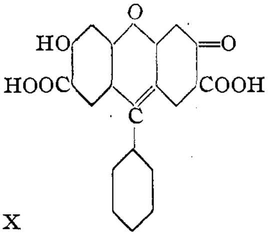
Analyses. Subs., 0.1200, 0.1110: CO_2, 0.3225, 0.2985; H_2O, 0.0394, 0.0361. Calc. for $C_{17}H_{10}O_4$: C, 73.40; H, 3.60. Found: C, 73.30, 73.34; H_2O, 3.65, 3.61.

9. **Resorcinol-*p*-hydroxy-*m*-carboxybenzein** (IX).—A mixture of 5 g. of the 5-aldehydo-salicylic acid (prepared by Cohen's modification of Reimer and Tieman's method[5]) with 8.8 g. of resorcinol was added to 20 cc. of sulfuric acid in a conical flask while it was constantly stirred. The mixture was heated on the water-bath for about an hour. At the end of the reaction the product was treated with ice-cold water, purified in the usual manner and obtained as a yellow powder; yield, 3 g. It dissolves in sodium hydroxide solution (red color, red-green fluorescence), in sulfuric acid (yellow color, no fluorescence), in alcohol (yellow color, no fluorescence) and in pyridine (reddish-yellow color, no fluorescence), and is insoluble in nitrobenzene, ether or benzene. It dyes wool and silk a bright yellow shade. It does not melt below 295°.

Analyses. Subs., 0.1300, 0.1350: CO_2, 0.3241, 0.3385; H_2O, 0.0409, 0.0428. Calc. for $C_{20}H_{12}O_6$: C, 68.96; H, 3.44. Found: C, 67.99, 68.38; H, 3.49, 3.52.



IX



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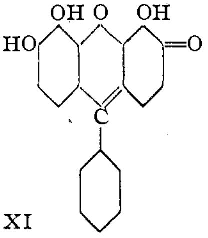

XI

10. **β-Resorcylic-acid-benzein** (X).—Five and six-tenths g. of β-resorcylic acid was condensed with 2.2 cc. of benzaldehyde in the same manner as in the case of re-

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[5] Wayne and Cohen, *J. Chem. Soc.*, **121**, 1022 (1922).

sorcinol-benzein. The usual method of purification was adopted, giving a yellow powder; yield, 2.5 g. It is soluble in sodium hydroxide solution (orange color, green fluorescence), in sulfuric acid (yellow color, no fluorescence) and in alcohol (orange-yellow color, no fluorescence).

Analyses. Subs., 0.1200, 0.1220: CO_2, 0.2944, 0.2997; H_2O, 0.0346, 0.0343. Calc. for $C_{21}H_{12}O_7$: C, 67.02; H, 3.19. Found: C, 66.91, 66.99; H, 3.20, 3.12.

11. **Resorcinol-3-methoxybenzein.**—A mixture of 4.4 g. of resorcinol, 2.5 cc. of anisaldehyde and 10 cc. of sulfuric acid was heated to 110–115° on an oil-bath for about an hour. The usual method of purification was adopted and the substance was obtained as a yellow powder. It does not melt or decompose below 285°. It dissolves in sodium hydroxide solution (red color, bluish fluorescence), in alcohol (yellow color, no fluorescence), in sulfuric acid (dark red color, no fluorescence) and in pyridine (light yellow color, no fluorescence), and is insoluble in ether or benzene. It dyes wool and silk from an acid bath a bright yellow shade.

Analyses. Subs., 0.1220, 0.1200: CO_2, 0.3367, 0.3308; H_2O, 0.0485, 0.0475. Calc. for $C_{20}H_{14}O_4$: C, 75.40; H, 4.40. Found: C, 75.27, 75.18; H, 4.41, 4.39.

TETRABROMO DERIVATIVE.—Five g. of the pure substance was brominated in the usual manner by the slow addition of 2.5 cc. of liquid bromine. The red precipitate thus obtained was crystallized from alcohol as a red powder. It is soluble in sodium hydroxide solution (deep red color, no fluorescence), in alcohol (reddish-orange color, greenish-orange fluorescence) and in concd. sulfuric acid (reddish-yellow color, no fluorescence). It does not melt, but decomposes at 200°, and dyes wool and silk a red shade.

Analysis. Subs., 0.1200: AgBr, 0.1421. Calc. for $C_{20}H_{10}O_4Br_4$: Br, 50.46. Found: 50.30.

12. **Pyrogallol-benzein** (XI).—A solution of 7.5 g. of pyrogallic acid in 20 cc. of concd. sulfuric acid was condensed with 3.15 cc. of benzaldehyde in the usual manner, and the product, purified as described above, obtained as a brown powder; yield, 2.5 g. It dissolves in sodium hydroxide (yellow solution, no fluorescence), in sulfuric acid (brownish-red solution, no fluorescence), in pyridine (red solution, no fluorescence), in nitrobenzene (red solution, no fluorescence). It does not melt below 295°.

Analyses. Subs., 0.1350, 0.1310: CO_2, 0.3516, 0.3419; H_2O, 0.0450, 0.0433. Calc. for $C_{19}H_{12}O_5$: C, 71.25; H, 3.75. Found: C, 71.03, 71.17: H, 3.70, 3.67.

Summary

1. Compounds of the type of benzeins have been obtained in good yields by the condensation of various aldehydes with resorcinol and other hydroxy compounds in the presence of concd. sulfuric acid at temperatures varying from 100° to 130°.

2. These compounds are more or less fluorescent, the intensity of fluorescence in sodium hydroxide solution varying with the number and the position of hydroxyl and carboxyl groups. Thus, (1) in the phenyl residue R, the *ortho* position to the central carbon atom is most favorable and the *meta* position is most unfavorable for the carboxyl group to excite fluorescence; (2a) in the phenyl residue R, the *ortho* and *para* positions to the central carbon atom are also favorable for the hydroxyl group, although the effect is not so marked as in the case of carboxyl groups; (2b) in the benzene nuclei associated with the pyrone ring, Position 6 or 3 is

most favorable and 4 and 5 positions are most unfavorable for hydroxyl groups; (3) the influence of hydroxyl groups on fluorescence is greater when they occur in the benzene nuclei than when they occur in the phenyl residue, whereas the influence of carboxyl groups is greater in the phenyl residue than in the benzene nuclei.

3. Bromo derivatives of these compounds which have been studied do not fluoresce in any other ordinary solvents except alcohol.

Calcutta, India

[Contribution from the Chemical Laboratory of the University of Washington]

SOME CACODYL DERIVATIVES

By Frank A. Lee, Curtis Thing and William M. Dehn

Received June 9, 1923

General

The classical investigations of Robert Bunsen in the cacodyl series have remained substantially free from revision[1] since their publication (1837–1843). This paper develops some new compounds of this series and also concerns itself with reinvestigations of some of Bunsen's compounds, for the purposes both of fixing their formulas and of improving their yields. Though some have been obtained through substitution and oxidation, most of the new compounds herein described are additive or are hydrolytic products of such additive compounds. It is of special interest to note that one chlorine atom of the pentavalent arsenic compounds is characteristically susceptible to hydrolysis.

Experimental Part

Cacodyl was prepared in large quantities by the usual method[2] and was then converted into cacodyl chloride[3] by the use of mercuric chloride. It boiled[4] at 109°.

Preparation of Cacodyl Bromide.[5]—Molecular quantities of potassium bromide and cacodyl chloride with 3 to 4 volumes of absolute alcohol were heated for 4 to 5 hours on a water-bath under a return condenser. Practical exclusion of air is advisable to avoid formation of the hydrated oxybromide. The reaction mixture was distilled from a sand bath as long as any distillate was obtained. The latter was treated with 5 to 10 volumes of water to precipitate the cacodyl bromide, which was then separated, dried with calcium chloride and fractionated. The yield of the bromide, boiling at 130°, was nearly quantitative.

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[1] Ostwald's "Klassiker der Exakten Wissenschaften," No. 27, pp. 138–148. Baeyer recalculated some of Bunsen's data with revised atomic weights and proposed some alternate formulas.

[2] (a) Bunsen, *Ann.*, **37**, 6 (1841); (b) **107**, 257 (1858). This Journal, **35**, 2 (1906).

[3] (a) Ref. 2a, p. 30; (b) *Ann.*, **42**, 22 (1842).

[4] Bunsen gave the boiling point as "over 100°."

[5] Ref. 2a, p. 33. Bunsen prepared this compound in accordance with the reaction, $[(CH_3)_2As]_2O + 2HgCl_2 + 2HBr \longrightarrow 2(CH_3)_2AsBr + 2HgCl_2 + H_2O$.