[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRESIDENCY COLLEGE, CALCUTTA]

THE CONDENSATION OF PRIMARY ALCOHOLS WITH RESORCINOL AND OTHER HYDROXY AROMATIC COMPOUNDS

BY RAJENDRA NATH SEN AND NRIPENDRA NATH SARKAR

RECEIVED SEPTEMBER 27, 1924 PUBLISHED APRIL 4, 1925

I. Benzeins, Naphthaleins and Glycereins

The present investigation was undertaken with a view to determine whether compounds of the type of benzeins like those obtained by the condensation of aldehydes with resorcinol and similar hydroxy compounds[1] can be obtained directly by the condensation of alcohols with resorcinol[2] and other similar aromatic hydroxy compounds with the help of a suitable condensing agent in the presence of an oxidizing substance.

Attention was first directed to finding suitable oxidizing and condensing agents. A number of oxidizing agents were tried and each was found to have defects. Nitrosyl sulfate was the first substance tried; it was found to give resorufin as one of the secondary products when resorcinol was used as the hydroxy compound. To separate this secondary product from the main product, namely, the benzein, was extremely difficult. Mixtures of manganese dioxide and sulfuric acid (d., 1.84) and of manganese dioxide, sodium chloride and sulfuric acid (d., 1.84) were next tried in succession at 100°, and it was found that the yield of the desired product was extremely poor. Potassium persulfate ($K_2S_2O_8$) dissolved in cold, concd. sulfuric acid (d., 1.84) was found to give satisfactory results, oxidation and condensation taking place simultaneously. Thus about 80% of the calculated yield of benzein was obtained by heating together one molecular equivalent of benzyl alcohol and two of resorcinol with the requisite quantity of potassium persulfate dissolved in sulfuric acid (d., 1.84) at 100°. It was then found that one-third (or even less) of the calculated quantity of potassium persulfate in the presence of concd. sulfuric acid would bring about the desired oxidation and condensation in a satisfactory manner when the reaction was carried out by heating at a temperature of 120° for two hours or so. It seemed possible, therefore, that the oxidation and condensation might be effected by sulfuric acid (d., 1.84) alone. This was found to be the case, the most favorable temperature for the reaction being 140–150°. When a mixture of two molecular equivalents of resorcinol and one of benzyl alcohol was heated to 140–150° with the calculated quantity of concd. sulfuric acid (d., 1.84) for six to seven hours, sulfur dioxide was evolved continuously and about 90% of the calculated yield of the benzein was obtained.

---

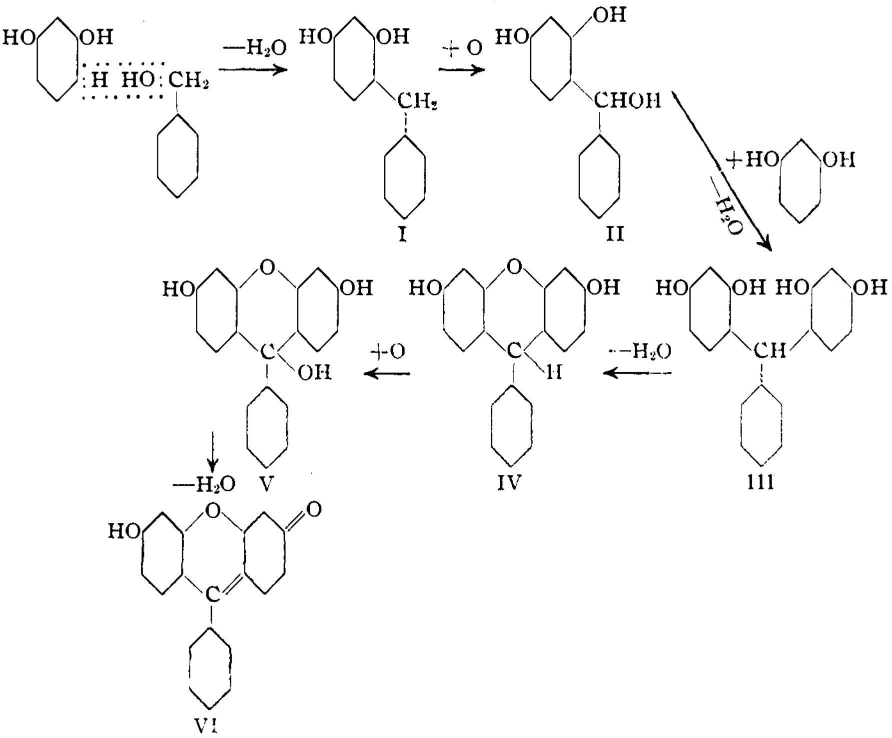
[1] Sen and Sinha, THIS JOURNAL, 45, 2988 (1923).

[2] For a description of the previous work on the condensation of alcohols with phenols, see Paterno and Fileti, *Gazz. chim. ital.*, 5, 381 (1875); *Chem. Zentr.*, **1903**, I, 288; Faget, *Ann.*, **124**, 356 (1862); Houston, THIS JOURNAL, **46**, 2775 (1924), and the references given in the last article.

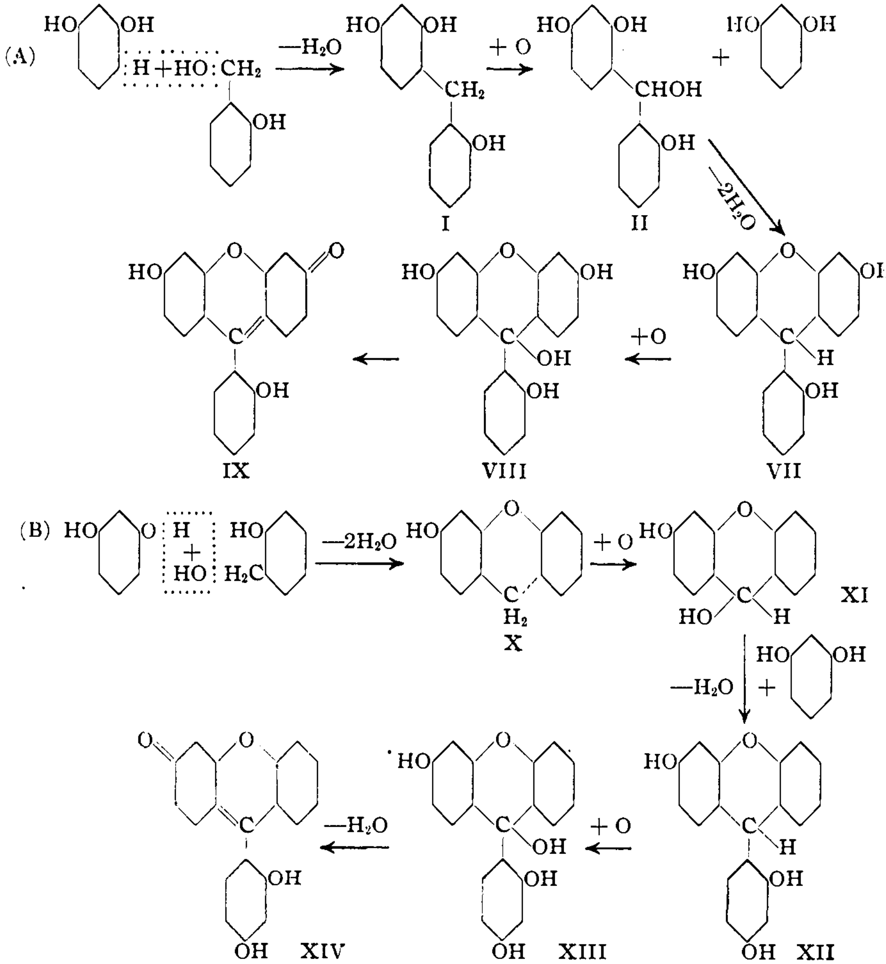
To prove that the reaction is of general application, the condensation of various alcohols with aromatic hydroxy compounds has been successfully effected in yields exceeding 80%, the details being given in the experimental part. One peculiarity in general must be mentioned here: the reaction in the case of the hydroxy alcohols takes place with greater ease and in less time than in the case of unsubstituted alcohols. In the case of the condensation of benzyl alcohol with gallic acid, potassium persulfate had to be used at 120°, since sulfuric acid alone at 140–150° gives rise to another substance, hexahydroxy-anthraquinone (rufigallol), by the condensation of two molecules of gallic acid.

The Mechanism of the Reaction

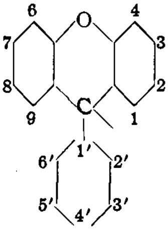
In the first stage of the reaction one molecular equivalent of the alcohol reacts with one of resorcinol. and a diphenylmethane derivative (I) is formed by the elimination of one molecule of water. This diphenylmethane derivative is then oxidized to a benzohydrol (II) which reacts with a second equivalent of resorcinol and gives rise to Product III. Next, one equivalent of water is eliminated, whereby a xanthene derivative is formed (IV). This xanthene derivative is then oxidized to a xanthydrol derivative (V) which by elimination of a molecule of water gives rise to the benzein (VI). The various stages may be represented thus.



In condensations with alcohols which have one hydroxyl group in the *ortho* position to the alcohol (CH_2OH) group, there should exist the possibility of the formation of two isomeric benzeins, as will be evident from the following representations of the condensation of *o*-hydroxybenzyl alcohol (saligenin) with resorcinol. In one case (A), pyrone ring formation may take place by the interaction of two hydroxyl groups in the two resorcinol molecules, whereas in the other case (B) the pyrone ring may be formed by the interaction of one hydroxyl group in the resorcinol molecule and one hydroxyl group in the alcohol molecule, thus:



In the first case the general course of the reaction (described above), takes place, the final product (IX) being resorcinol-*o*-hydroxybenzein, whereas in the second case a xanthene derivative (X) is first formed by the elimination of two molecules of water from one molecule of the alcohol and one molecule of resorcinol. This is then oxidized to a xanthydrol (XI) which condenses with a second molecule of resorcinol. The product (XII) is again oxidized to a xanthydrol derivative (XIII) which by the elimination of a molecule of water gives rise to a fluorone derivative (XIV), which is 2′,4′-dihydroxyphenyl-fluorone, the numbering being shown below



It is interesting to note that both isomeric compounds have actually been obtained, the second (XIV) being the main product, as will be seen later.

The formation of the first isomeric compound (IX) can be completely eliminated by preparing the xanthene derivative (X) first and then condensing the resulting compound with a second molecule of resorcinol in the presence of an oxidizing agent. (See p. 1084.)

The first isomeric compound (IX) is formed in only small quantity under the conditions described in the experimental part, and this isomer was found to be identical with resorcinol-*o*-hydroxybenzein, first prepared by Sen and Sinha.[3] Reichl[4] obtained "glycereins" by the condensation of glycerol with phenol, resorcinol, pyrogallol, etc. He explained the formation of phenol-glycerol according to the equation, $C_6H_6O + C_3H_8O_3 = C_9H_{10}O_2 + 2H_2O$. The author attempted to condense glycerol with resorcinol in order to determine the nature of Reichl's product, and the possibility of obtaining pyronine dyes in good yield. Accordingly, two molecular equivalents of resorcinol and one of glycerol were heated with the required quantity of concd. sulfuric acid (d., 1.84) at 130–150° for four hours; sulfur dioxide was freely evolved and the characteristic odor of acrolein was also noticed; yield of mixed material, 75%. The product consisted of two distinct compounds, one of which has been termed resorcinol-glycerein in accordance with Reichl's method of nomenclature, although he attributed a different constitution to the product; the other has been named resorcinol-acrolein. In this connection it might be mentioned that the temperature of 130–140° was favorable to a good yield of the glycerein, whereas that of 140–150° or above gave a better yield of the acrolein.

---

[3] Ref. 1, p. 2990.

[4] Reichl, *Dingler's polytech. J.*, **235**, 532; *Ber. Österr. Chem. Ges.*, **1879**, 12; *J. Chem. Soc.*, **38**, 426 (1880).

The acrolein was prepared alone by heating one molecular equivalent of glycerol with two of resorcinol in the presence of potassium hydrogen sulfate and concd. sulfuric acid at 140–150° for three to four hours; yield, about 80%.

The constitutions assigned to these products are based on the mode of their formation and supported mainly by the results of their analyses. The compounds have the quinonoid structure, as will be evident from the analyses of the potassium salts. Their benzoyl derivatives also lend support to this view. The bromine derivatives are mostly tetrabromo compounds, although dibromo derivatives have been obtained in a few cases. The fluorescence of these compounds varies from yellow-green to orange-green and the colors of their bromo derivatives vary from red to violet-red.

II. Xanthenes and Fluorones

In connection with the study of the condensation of alcohols with aromatic hydroxy compounds, it was observed that besides the compounds of the type of benzeins already described, a series of interesting products, namely, xanthenes, could be obtained very easily and in good yields by the condensation of *o*-hydroxy alcohols with resorcinol and similar hydroxy compounds in the presence of anhydrous zinc chloride.

These xanthene derivatives are generally prepared by the reduction of the corresponding xanthones.[5] They have also been obtained by the condensation of *m*-dihydroxy- or *m*-aminophenols with formaldehyde or with methylene chloride,[6] and the subsequent treatment of the products with zinc chloride or phosphorus oxychloride. F. G. Pope[7] mentions the formation of the simplest xanthene by the condensation of *o*-cresol with phenol by means of anhydrous aluminum chloride.

In the present method, one molecular equivalent of the hydroxy alcohol is heated with one equivalent of resorcinol or β-naphthol in the presence of anhydrous zinc chloride at 140–160°. Thus, saligenin with resorcinol yielded 3-monohydroxy-xanthene; β-hydroxynaphthyl carbinol gave 3-monohydroxy-phenylnaphtho-xanthene with resorcinol, and β,β′-dinaphthoxanthene with β-naphthol, and so on. Most of these compounds appear not to have been prepared before.

Attempts were also made to bring about the condensation described above by means of concd. sulfuric acid (d., 1.84) at 100°, instead of with anhydrous zinc chloride at a higher temperature. The products thus obtained always contained lower percentages of carbon and hydrogen. This may be attributed to the formation of a small amount of the fluorone compounds by the partial oxidation of the xanthene derivatives at the expense of the concd. sulfuric acid, or to the formation of a small amount

---

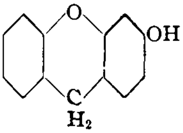
[5] Dreher and v. Kostanecki, *Ber.*, **26**, 72 (1893).

[6] Wolff, *Ber.*, **26**, 84 (1893).

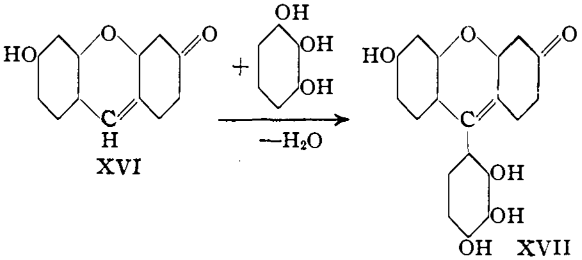
[7] Pope, "Modern Researches in Organic Chemistry," p. 271.

of the benzein derivative by the partial oxidation of the xanthene to the xanthydrol and the subsequent condensation of the xanthydrol with the hydroxy compound by means of concd. sulfuric acid.

These xanthene and fluorone derivatives have been further condensed with a second molecule of resorcinol or some other hydroxy compound by means of concd. sulfuric acid (d., 1.84), whereby compounds of the type of benzeins have been obtained. Thus 3-hydroxyxanthene (XV) gave rise to 2′,4′-dihydroxyphenyl-fluorone with resorcinol; 6-hydroxyfluorone (XVI) gave rise to resorcinol-*o,m,p*-trihydroxybenzein (XVII) with pyrogallol.



XV



XVI

XVII

The above reaction has lent a direct additional support to the view regarding the course of the reaction followed in the case of the formation of the isomeric compounds of the benzeins.

Experimental Part

I. Benzeins

The preparation of resorcinol-benzein is typical. A mixture of 2.2 g. of freshly distilled benzyl alcohol and 4.5 g. of resorcinol was heated with 5 cc. of concd. sulfuric acid (d., 1.84) at 140–150° for six hours. Sulfur dioxide was evolved and the mass became semi-solid. The product was washed with cold water, dissolved in dil. sodium hydroxide solution, the alkaline solution filtered and precipitated by dil. hydrochloric acid. The above operation was repeated and finally the product was thoroughly washed with cold water. The product was next dissolved in hot, 95% alcohol and the solution cooled, yielding a yellow powder that was recrystallized from hot nitrobenzene.

For the preparation of resorcinol-*o,p*-dihydroxybenzein, *o,p*-dihydroxybenzyl alcohol ($C_7H_8O_3$), which appears not to have been prepared heretofore, was obtained by Manasse's method as follows. Five g. of resorcinol was dissolved in 100 cc. of a 1% solution of sodium hydroxide. To this solution at 0–5° was added 10 cc. of a 40% solution of formaldehyde. The solution was kept at this temperature for an hour or so, during which it acquired a light red color. It was then treated with dil. acetic acid, whereupon a white precipitate was obtained which was thoroughly washed with cold water, dissolved in absolute alcohol and the alcoholic solution was poured into water, a white precipitate being obtained which was dried in a vacuum desiccator. It changes readily to a brick-red powder that is insoluble in alcohol. It is sparingly soluble in acetone and glacial acetic acid, but insoluble in benzene, ether and chloroform.

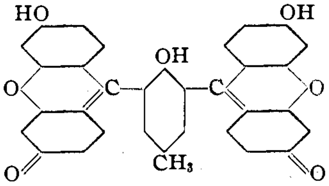
Anal. Calcd.: C, 60.0; H, 5.7. Found: C, 59.7; H, 6.0.

The benzeins prepared, together with their derivatives, are listed in Table I.

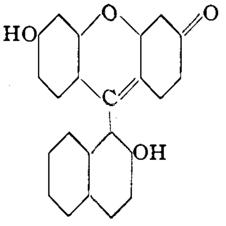
II. Naphthalein

Resorcinol-β-hydroxynaphthalein, XVIII.—A mixture of 3.5 g. of β-hydroxynaphthyl carbinol (prepared by Manasse's method from β-naphthol) and 4.5 g. of resorcinol was heated to 130–140° for four to five hours. The subsequent process of purification was similar to that for resorcinol-*o*-hydroxybenzein. The portion insoluble in alcohol 2',4'-dihydroxyphenyl-naphthophenylfluorone, is described on p. 1090. The alcoholic extract yielded 1.5 g. of an orange-red powder that did not melt below 250°. It dyes wool and silk an orange shade. It dissolves in alkali forming an orange solution with a greenish-blue fluorescence. It is soluble in alcohol, acetone and in pyridine, but insoluble in ether, benzene and glacial acetic acid.

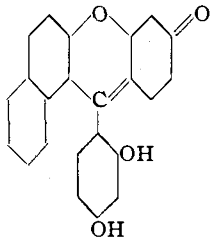
Anal. Calcd. for $C_{23}H_{14}O_4$: C, 77.9; H, 3.98. Found: C, 77.46; H, 4.3.



XVIII



XIX



XX

The tetrabromo derivative dissolves in alkali without fluorescence, and dyes wool a shade redder than that given by resorcinol-*o*-hydroxybenzein.

Anal. Calcd. for $C_{23}H_{10}O_4Br_4$: Br, 47.7. Found: 47.5.

III. Glycereins

A. Resorcinol-glycerein.—A mixture of 2 g. of glycerol and 4.6 g. of resorcinol was heated to 130–150° with 5 cc. of concd. sulfuric acid for four to five hours. Sulfur dioxide was evolved and the odor of acrolein was also noticed. After the usual acid-alkali treatment the product was treated with 95% alcohol, in which a portion was soluble. The insoluble portion, resorcinol-acrolein, is described on p. 1088. The alcoholic extract was poured into acidified water, a red powder being obtained which was finally crystallized from hot 95% alcohol; m. p., above 250°. It is very soluble in alcohol and acetone and it dissolves in alkali forming a red solution with a green fluorescence. It is insoluble in ether, benzene and chloroform.

Anal. Calcd. for $C_{15}H_{12}O_5$: C, 66.17; H, 4.41. Found: C, 65.9; H, 4.5.

TABLE I

BENZEINS

Name -benzein	Formula	Method of preparation	M. p. °C.	Analysis				Properties
				C		H		
				Calcd. %	Found %	Calcd. %	Found %	
Resorcinol-[a]	$C_{19}H_{12}O_3$	Benzyl alcohol + resorcinol + concd. H_2SO_4 at 140–150°.		79.16	79.01	4.10	4.18	Red, microcrystalline, from hot nitrobenzene.
Benzoyl deriv.	$C_{19}H_{11}O_2OOC.C_6H_5$		141	79.4	79.4	4.08	4.3	Light yellow, microcrystalline.
Potassium salt	$C_{19}H_{11}O_3K$				K, 11.99	11.8		
Tetrabromo compd.	$C_{19}H_8O_3Br_4$				Br, 53.0	52.6		Decomposes without melting.
Resorcinol-*o*-hydroxy-	$C_{19}H_{12}O_4$ (IX)	Saligenin[b] + resorcinol + concd. H_2SO_4 at 140–150°.	Above 250	75.0	74.7	3.94	4.12	Blue fluorescence, orange color in alkaline solution. Dyes orange shades on wool.
Potassium salt	$C_{19}H_{10}O_4K_2$				K, 20.53	20.92		
Tetrabromo compd.	$C_{19}H_{10}O_4Br_4$				Br, 51.58	51.1		
Resorcinol-*o,p*-dihydroxy-	$C_{19}H_{12}O_5$	*o,p*-Dihydroxy-benzyl alcohol + resorcinol.	Above 250	71.25	71.0	3.75	3.9	Orange - red powder. Green fluorescence and orange color in alkaline solution. Gives orange shades on wool.
Tetrabromo compd.	$C_{19}H_8O_5Br_4$		Decomp. above 170 w.o. melting		Br, 50.3	50.2		Non-fluorescent in dil. alkaline soln.
Resorcinol-*m*-nitro-*p*-hydroxy-	$C_{19}H_{11}O_6N$	*m*-nitro-*p*-hydroxybenzyl alcohol[c] + resorcinol.	above 250		N, 4.0	3.94		Red in alkaline soln. with green fluorescence. Gives orange shades on wool.
Potassium salt	$C_{19}H_9O_6NK_2$				K, 18.9	18.9		
?	$C_{33}H_{20}O_7$	1-Hydroxy-4-methylphenyl-2,6-dicarbinol[d] + resorcinol.	Above 250	75.0	74.8	3.6	3.8	Sparingly sol. in 95% alcohol; readily sol. in pyridine. Dyes wool a light orange shade.

Table I (*Concluded*)

Name -benzein	Formula	Method of preparation	M. p. °C.	Analysis				Properties
				C		H		
				Calcd. %	Found %	Calcd. %	Found %	
Resorcinol-*o*,*m*,*p*-trihydroxy-	$C_{19}H_{12}O_6$[c]	6-Hydroxyfluorone + pyrogallol + H_2SO_4 at 140–150° for 3–4 hours.	Above 230	67.8	67.5	3.57	3.67	Purified like resorcinol-benzein; red powder from 95% alcohol. Sol. in alkali, giving red soln. with green fluorescence. Sol. in alcohol, acetone, pyridine; insol. in benzene and glacial acetic acid.
Resorcinol-*m*-carboxylic-*p*-hydroxy-	$C_{20}H_{12}O_6$	6-Hydroxyfluorone + salicylic acid.	Above 250	68.96	68.8	3.44	3.62	Similar to the compound obtained by condensing 5-aldehydo-salicylic acid with resorcinol (Ref. 1, p. 2994).
Pyrogallol-	$C_{19}H_{12}O_5$	Benzyl alcohol + pyrogallol.		71.25	71.06	3.75	3.8	Blackish-brown.[e]
Pyrogallol-*o*-hydroxy-	$C_{19}H_{12}O_6$	Saligenin + pyrogallol.	Above 250	67.8	67.5	3.57	3.69	Black powder. Sol. in alcohol, acetone, pyridine and concd. H_2SO_4 without fluorescence.
Gallic acid-	$C_{21}H_{20}O_9$	Benzyl alcohol + gallic acid.		61.67	61.20	2.94	3.2	Light green powder.[f]

---

[a] This compound has been prepared by other workers by different methods: from benzotrichloride and resorcinol [Döbner, *Ann.*, **217**, 234 (1883)]; from benzoic acid and resorcinol [Cohn, *J. prakt. Chem.*, [II] **48**, 387 (1898)]; from 4-amidophenyl-fluorone [Kehrmann, *Ann.*, **372**, 294 (1910)]; from 2,4-dihydroxy-benzohydrol [Pope and Howard, *J. Chem. Soc.*, **97**, 1023 (1910)]; from benzaldehyde and resorcinol (Ref. 1, p. 2990).

[b] Prepared from phenol by the method of Manasse [*Ber.*, **27**, 2409 (1894)].

[c] Prepared from *o*-nitrophenol by the method of Manasse [*Ber.*, **34**, 2455 (1901); *Chem. Zentr.*, **1906**, II, 894)].

[d] Prepared from *p*-cresol by Manasse's method.

[e] The properties of this compound were identical with those of the compound obtained by Sen and Sinha (Ref. 1, p. 2995) by the condensation of benzaldehyde and pyrogallol.

[f] Properties identical with those of the compound prepared by Sen and Sinha (Ref. 1, p. 2992).

On benzoylation a brownish-yellow powder was obtained which was found to be a tribenzoyl derivative.

Anal. Calcd. for $C_{15}H_9O_2(OCOC_6H_5)_3$: C, 73.9; H, 4.1. Found: C, 73.4; H, 4.35.

The bromine derivative was a dibromo compound.

Anal. Calcd. for $C_{15}H_{10}O_5Br_2$: Br, 37.2. Found: 37.8.

B. **Pyrogallol-glycerein.**—A mixture of 2 g. of glycerol and 5.1 g. of pyrogallol was heated to 130–150° for four to five hours with .7 cc. of concd. sulfuric acid (d., 1.84). The product was purified as was resorcinol-glycerein. The pyrogallol-glycerein was obtained from the alcoholic extract as a brown powder; m. p., above 250°. The residue insoluble in 95% alcohol, pyrogallol-acrolein, is described under acroleins. Pyrogallol-glycerein is soluble in acetone, pyridine and concd. sulfuric acid without fluorescence.

Anal. Calcd. for $C_{15}H_{12}O_7$: C, 59.2; H, 3.94. Found: C, 58.8; H, 4.17.

IV. Acroleins

A. **Resorcinol-acrolein.**—This compound was obtained in the preparation of resorcinol-glycerein. The portion that was insoluble in 95% alcohol was dissolved in pyridine and allowed to crystallize; a yellow-orange powder was obtained; m. p., above 250°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Found: C, 75.3; H, 4.4. Calcd. for $C_{15}H_9O_3K$: K, 14.1. Found: 14.8.

B. **Pyrogallol-acrolein.**—This compound was obtained as the product insoluble in 95% alcohol in the preparation of pyrogallol-glycerein. It was purified by crystallization from dil. pyridine solution, as a black powder, non-fluorescent in all solvents; m. p., above 250°. It is insoluble in alcohol, acetone and benzene.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.6; H, 3.71. Found: C, 66.1; H, 3.86.

V. Xanthenes

The preparation of 3-hydroxyxanthene (XV) is typical. A mixture of 2.5 g. of saligenin and 2.2 g. of resorcinol was heated with 1 g. of anhydrous zinc chloride at 140–150° for two to three hours. The product was cooled and washed with hot water, acidified with hydrochloric acid, and the precipitate purified as in the case of resorcinol-benzein.

The xanthenes prepared are listed in Table II.

VI. Fluorones

Fluorone (6-Hydroxyfluorone) (ZVI).—Two and eight-tenths g. of *o,p*-dihydroxybenzyl alcohol and 2.2 g. of resorcinol were heated with 1 g. of zinc chloride at 160–180° for two to three hours. The product was washed with hot water, dissolved in sodium hydroxide solution and a current of air was then passed through the alkaline solution for eight to ten hours to complete the partial oxidation of the xanthene to fluorone. The alkaline solution was next precipitated by dil. hydrochloric acid and the product thus obtained was purified from alcohol. Its properties were identical with the compound obtained by Mohlau and Koch.[8]

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.5; H, 3.71. Found: C, 73.2; H, 3.97.

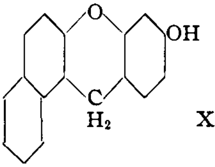
---

[8] Mohlau and Koch, *Ber.*, **27**, 2887 (1894).

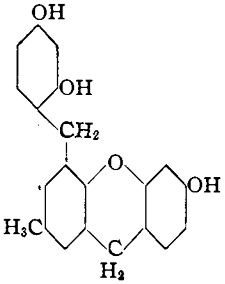
TABLE II
XANTHENES

				Analysis				
				C		H		
Name -xanthene	Formula	Method of preparation	M. p. °C.	Calcd. %	Found %	Calcd. %	Found %	Properties
3-Hydroxy-	$C_{13}H_{10}O_2$ (XV)	Saligenin + resorcinol + $ZnCl_2$ at 140–150° for 2–3 hours.	61	78.78	78.5	5.05	5.2	Yellow powder, changing to orange-red on exposure to air. Sol. in alkali with orange-red color and without fluorescence. Sol. in alcohol, acetone; insol. in benzene and chloroform.
Dibromo compd.			217 w. decomp..					
3-Hydroxyphenyl-naphtho-	$C_{17}H_{11}O_2$ (XXI)	β-Hydroxy-naphthyl carbinol + resorcinol + $ZnCl_2$ at 160–180° for 2–3 hours.	122	82.26	81.8	4.83	5.04	Orange-red solution in alkali, with feeble green fluorescence. Sol. in alcohol. ether, pyridine; sparingly sol. in chloroform; insol. in glacial acetic acid.
3-Hydroxy-5-di-, hydroxy-benzyl-7-methyl-	$C_{21}H_{18}O_4$ (XXII)	1-Hydroxy-4-methylphenyl-2,6-diol + resorcinol + $ZnCl_2$ at 150–160° for 2–3 hours	Above 250	75.4	75.1	5.38	5.51	Light red powder. Sol. in alkali without fluorescence. Sol. in alcohol. acetone. pyridine: insol. in benzene and glacial acetic acid.
β,β′-Dinaphtho-[a]	$C_{21}H_{14}O$	β-Hydroxy-naphthyl carbinol + β-naphthol + $ZnCl_2$ at 160–180° for 3–4 hours.	199	89.3	89.0	4.96	5.2	Light green, microcrystalline powder from glacial acetic acid. Insol. in sod. hydroxide soln. Sol. in concd. sulfuric acid with orange-red color and green fluorescence. Sol. in alcohol, glacial acetic acid; sparingly sol. in acetone.

[a] This compound has been previously obtained from β-naphthol and formaldehyde (Ref. 6).



XXI



XXII

2′,4′-Dihydroxyphenyl-fluorone.—This compound was obtained in the preparation of resorcinol-*o*-hydroxybenzein. The product (XIV) insoluble in 95% alcohol was dissolved in dil. pyridine and the pyridine solution yielded 3.7 g. of a light orange-red powder which dissolved in alkali giving a red solution with a faintly green fluorescence; m. p., above 250°. It dyes wool a deeper shade (redder) than its isomer, resorcinol-*o*-hydroxybenzein.

Anal. Calcd. for $C_{19}H_{12}O_4$: C, 75.0; H, 3.94. Found: C, 74.6; H, 4.3.

A mixture of 3 g. of 3-hydroxyxanthene and 2 g. of resorcinol was heated to 140–150° with 5 cc. of concd. sulfuric acid (d., 1.84) for two to three hours. The product was purified in the usual manner.

Anal. Calcd. for $C_{19}H_{12}O_4$: C, 75.0; H, 3.9. Found: C, 74.6; H, 4.2.

2′,4′-Dihydroxy-phenylnaphtho-phenylfluorone, XX.—This product was obtained as the portion insoluble in alcohol in the preparation of resorcinol-β-hydroxynaphthalein. It's precipitate from dil. pyridine was orange-red. It is insoluble in alcohol, benzene and glacial acetic acid; m. p., above 250°. It dyes wool an orange-red shade.

Anal. Calcd. for $C_{23}H_{14}O_4$: C, 77.9; H, 3.98. Found: C, 77.5; H, 4.27.

The bromine derivative, prepared in ice-cold alkaline solution, was found to be a dibromo compound.

Anal. Calcd. for $C_{23}H_{12}O_4Br_2$: Br, 31.05. Found: 31.3.

Summary

1. The condensation of primary alcohols with resorcinol and other similar hydroxy compounds by means of concd. sulfuric acid (d., 1.84) at 140–150° has furnished an easy and efficient method for preparing the benzeins and the naphthaleins in good yields.

2. The xanthenes and the fluorones have been obtained in good yield by the condensation of equimolecular equivalents of the hydroxy alcohols and resorcinol or other similar hydroxy compounds by means of anhydrous zinc chloride at 140–180°. These xanthenes and fluorones have been further condensed with a second equivalent of an hydroxy compound in the presence of concd. sulfuric acid, whereby compounds of the type of benzeins have been obtained.

3. A further study has been made of the "glycereins" first prepared by Reichl. These compounds have been prepared at 130–150° in the presence of concd. sulfuric acid, acroleins being obtained simultaneously. They

can be separated by crystallization from 95% alcohol in which the glycereins are soluble. These compounds have been found to be pyronine dyes.

4. A close study of the fluorescence of the benzeins and the naphthaleins has shown that there is no appreciable difference in their fluorescence in dil. alkaline solutions, but the naphthaleins dye a deeper shade than the benzeins. The glycereins with aliphatic groups in place of the phenyl residues of the benzeins show fluorescence similar to that of the benzeins but dye weaker shades, whereas the acroleins have a faint green fluorescence and have practically no tinctorial properties. The pyrogallol and the gallic acid compounds dye brown to blackish-brown shades; the former have no fluorescence in any solvent, whereas the latter show a strong green fluorescence in concd. sulfuric acid.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

PREPARATION AND PROPERTIES OF DICHLORO-ACETIC ACID

BY HOWARD WATERS DOUGHTY AND ARTHUR PROCTOR BLACK

RECEIVED OCTOBER 21, 1924 PUBLISHED APRIL 4, 1925

Dichloro-acetic acid has been prepared in a variety of ways, of which the following are the most important.

Maumené[1] obtained it by direct chlorination of monochloro-acetic acid. Müller[2] by chlorination of acetic acid in presence of iodine. Wallach[3] by the action of potassium cyanide on chloral in aqueous solution. Brand[4] by electrolytic reduction of trichloro-acetic acid. In 1922 Doughty and Freeman[5] found that dichloro-acetic acid is formed when copper powder and trichloro-acetic acid react in benzene or aqueous solution and that tetrachloro-succinic acid is also formed in small quantity when the reaction takes place in ether or without any solvent. They also prepared ethyl tetrachloro-succinate from ethyl trichloro-acetate and copper powder.

This investigation was undertaken to determine the conditions for maximum yield of dichloro-acetic acid by the method of Doughty and Freeman, and also to determine some of the physical constants of this acid, both as criteria of the purity of the acid thus obtained and on account of the fact that considerable discrepancy exists in the boiling point of the acid as recorded by various observers.

It was soon found that the reaction requires more copper than was used by Doughty and Freeman. They used three molecular equivalents of copper to two of trichloro-acetic acid, and when this proportion is used trichloro-acetic acid is always found in the product; but when two equiva-

---

[1] Maumené, *Compt. rend.*, **59**, 84 (1864); *Ann.*, **133**, 154 (1865).

[2] Müller, *Ann.*, **133**, 159 (1865).

[3] Wallach, *Ann.*, **173**, 295 (1874).

[4] Brand, Ger. pat. 246,661 (1911).

[5] Doughty and Freeman, THIS JOURNAL, **44**, 636 (1922).