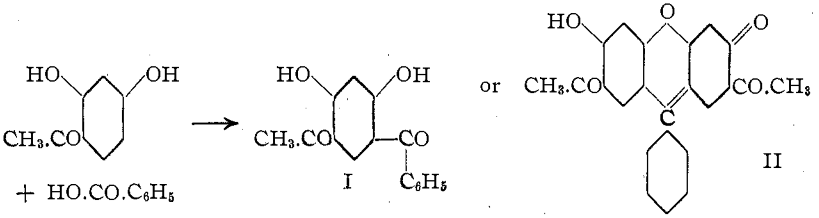
[Contribution from the Chemical Laboratory, University of Science, Calcutta]

THE CONDENSATION OF BENZOIC ACID AND SUBSTITUTED BENZOIC ACIDS WITH RESACETOPHENONE

By Gopâl Chandra Chakravarti

Received February 12, 1923

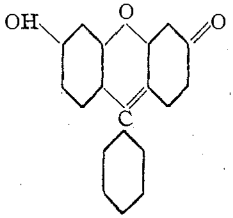
No condensation of resacetophenone with the benzoic acids seems to have been attempted. The reaction might proceed in a two-fold direction, yielding products belonging either to the benzophenone or to the benzein series, thus,



I

II

Cohn[1] prepared a fluorescent dye by heating resorcinol with benzoic acid in the presence of anhydrous zinc chloride, to which a number of erroneous formulas were assigned by many workers; but recently F. G. Pope[2] proved that the compound was a true benzein with the structure,



In the case of resacetophenone, also, it has been found that benzein derivatives (II) are invariably formed with the complete exclusion of I.

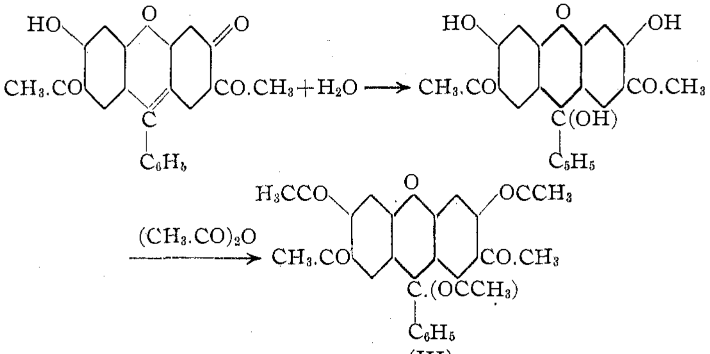
The compounds described in this paper are prepared by heating two molecules of resacetophenone with slightly more than one molecule of the acid in the presence of an excess of fused and anhydrous zinc chloride at an optimum temperature for different periods of time with different acids. As resacetophenone is partially decomposed into tarry products at the temperature of the reaction, the isolation of the dye is attended with considerable difficulties. The products show strong fluorescence in solutions in alkali, the tint varying from orange to red-green. They give unstable hydrochlorides with hydrochloric acid in glacial acetic acid solution. They invariably crystallize with one to four molecules of water of crystallization. The water can be only partially driven out by heating.

---

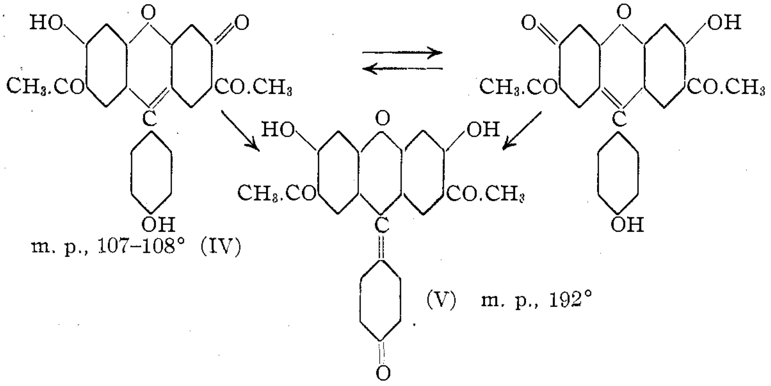
[1] Cohn, *Ber.*, **24**, 2064 (1891).

[2] Pope, *J. Chem. Soc.*, **105**, 251 (1914).

With acetic anhydride the benzeins are converted into acetyl derivatives, which are found to be colorless. Evidently, the quinonoid structure is lost by hydration through the water of crystallization.


(III)

The compound obtained by the condensation of resacetophenone with *p*-hydroxybenzoic acid shows some interesting properties. The freshly prepared product melts at 107–108°, but after several days the melting point changes to 192°. The two compounds are of the same color and their composition is the same. The compound melting at 192° does not revert to that melting at 107–108° when recrystallized from water. Loss of water of crystallization cannot, therefore, be the cause of the transformation. It is supposed that one of the compounds is the "homochromoisomer"[3] of the other.


m. p., 107–108° (IV)

(V) m. p., 192°

The condensation seems to take place very readily in the case of hydroxybenzoic acids, whereas it is difficult with nitro and halogenated acids, and the products of reaction in the latter case are comparatively small. No products of condensation could be isolated from *p*-toluic, 2-chlorobenzoic, 1,2,4- and 1,3,5-dinitrobenzoic acids on the one hand and resacetophenone on the other.

---

[3] Hantzsch, *Ber.*, **43**, (1910); **44**, 2001 (1911).

Experimental Part

Condensation of Resacetophenone with Benzoic Acid. II.—Six g. (two molecular equivalents) of resacetophenone was intimately mixed with 38 g. (more than one equivalent) of benzoic acid and 10 g. of powdered and fused zinc chloride. The mixture was heated in an oil-bath at a temperature of 140-145° for two hours and constantly stirred. The melt was poured into hot water whereby a tarry product was obtained. The separation of the dye from the tar presented much difficulty. It was effected by repeated crystallization from hot water and filtration by using a filter pump. The product thus purified was washed carefully with sodium acetate solution in order to get rid of the excess of benzoic acid and twice recrystallized from hot water. Beautiful rose-red crystals (m. p., 141°) were obtained after the final crystallization from chloroform. This product shows rose-green fluorescence in alkaline solution.

Analysis. Calc. for $C_{23}H_{16}O_5.4H_2O$: C, 62.2; H, 5.4. Found: C, 62.15; H, 5.2.

Acetylation (III).—One g. of the dye was dissolved in 10 cc. of acetic anhydride, and a few drops of pyridine were added to the solution. The mixture, after being gently boiled for an hour, was poured into water. When the water was evaporated, colorless prismatic crystals were left behind; m. p., 125°.

Analysis. Calc. for $C_{29}H_{24}O_9.H_2O$: C, 65.2; H, 4.9. Found: C, 64.94; H, 4.86.

Condensation of *p*-Hydroxybenzoic Acid with Resacetophenone.—IV.—Three g. of resacetophenone, 1.8 g. of *p*-hydroxybenzoic acid and 5 g. of fused zinc chloride were heated at 150–155° for an hour and a half. The melt was poured into water, separated from adhering tar by repeated crystallization from water, washed free from acid by means of sodium acetate solution and then recrystallized from water; m. p., 107–108°.

Analysis. Calc. for $C_{23}H_{16}O_6.4H_2O$: C, 60.00; H, 5.2. Found: C, 59.94; H, 5.3.

When the product melting at 107–108° was kept for a few weeks the melting point changed to 192° (V). This change was brought about more rapidly by keeping the substance in a vacuum over sulfuric acid for two or three days. The dye dissolves in alkali and the solution shows orange-green fluorescence.

Analysis. Calc. for $C_{23}H_{16}O_6.4H_2O$: C, 60.00; H, 5.2. Found: C, 59.88; H, 5.2.

Acetylation (Compare III).—One g. of the dye was mixed with 10 cc. of acetic anhydride and a few drops of pyridine, and the mixture gently boiled for 45 minutes and poured into water. The solution was filtered and concentrated, when shining rectangular plates separated. They were twice recrystallized from acetic acid; m. p., 102°.

Analysis. Calc. for $C_{31}H_{26}O_{11}.H_2O$: C, 62.8; H, 4.7. Found: C, 62.6; H, 4.9.

Condensation of Salicylic Acid with Resacetophenone.—A mixture of 1.8 g. of salicylic acid, 3 g. of resacetophenone and 6 g. of zinc chloride was heated for an hour and a half at 137–140°. On purification and crystallization as before, the product melted at 133–135°. It shows pink-green fluorescence in alkaline solution.

Analysis. Calc. for $C_{23}H_{16}O_6.4H_2O$: C, 60.00; H, 5.2. Found: C, 59.8; H, 5.1.

Acetylation.—The acetyl derivative was prepared as in other cases, and melted at 128°.

Analysis. Calc. for $C_{31}H_{26}O_{11}.H_2O$: C, 62.8; H, 4.7. Found: C, 62.6; H, 4.8.

Condensation of *p*-Nitrobenzoic Acid with Resacetophenone.—A mixture of 2 g. of *p*-nitrobenzoic acid, 3 g. of resacetophenone and 5 g. of zinc chloride was heated at 160° for two hours. The product was thoroughly washed with water and then with sodium acetate solution. The residue was treated with sodium carbonate solution, and the insoluble mass from the latter was dissolved in sodium hydroxide. On acidification with hydrochloric acid a product was obtained that melted above 300°.

Analysis. Calc. for $C_{23}H_{15}O_7N.H_2O$: C, 63.4; H, 3.9. Found: C, 63.1; H, 3.8.

Condensation of *m*-Nitrobenzoic Acid with Resacetophenone.—The same quantities of materials as in the case of *p*-nitrobenzoic acid, heated and purified in an identical manner, gave a product which did not melt below 290°.

Analysis. Calc. for $C_{23}H_{15}O_7N.H_2O$: C, 63.4; H, 3.9. Found: C, 63.3; H, 3.7.

Condensation of Anisic Acid and Resacetophenone.—A mixture of 1.8 g. of anisic acid, 3 g. of resacetophenone and 5 g. of zinc chloride was heated to 140° for about an hour. The product was purified from admixed tar, washed with sodium acetate solution and then dissolved in hot water. The precipitate that was obtained while the mother liquor was still hot was further crystallized from dilute alcohol; m. p., 161°.

Analysis. Calc. for $C_{24}H_{18}O_6.2H_2O$: C, 65.7; H, 5.02. Found: C, 65.47; H, 4.9.

Condensation of *m*-Bromobenzoic Acid with Resacetophenone.—*m*-Bromobenzoic acid (2.2 g.) was similarly treated with resacetophenone (3 g.) and the mixture heated to 145–150° for an hour. The product after purification and crystallization as before melted at 147°.

Analysis. Calc. for $C_{23}H_{15}O_5Br.H_2O$: Br, 17.06. Found: 16.92.

Condensation of *p*-Chlorobenzoic Acid with Resacetophenone.—Two g. of the acid was condensed with 3 g. of resacetophenone by heating for two hours at 165°. On purification as in the case of *p*-nitrobenzoic acid a product was obtained which did not melt below 300°.

Analysis. Calc. for $C_{23}H_{15}O_5Cl.H_2O$: Cl, 8.4. Found: 8.2.

Condensation of Gallic Acid with Resacetophenone.—A mixture of 2 g. of gallic acid, 3 g. of resacetophenone and 6 g. of zinc chloride was heated for 15–20 minutes at 160–165°. The melt was digested with water and the solution filtered when cool. The residue was dissolved in hot water and as the solution cooled, shining, brownish-red crystals were deposited; m. p., 126°.

Analysis. Calc. for $C_{23}H_{16}O_8.2H_2O$: C, 60.5; H, 4.4. Found: C, 60.7; H, 4.3.

In conclusion, the author's best thanks are due to Dr. P. C. Ghosh for his valuable help and to Sir P. C. Ray for his kind interest and encouragement.

Summary

1. The dyes obtained by the condensation of resacetophenone with free and substituted benzoic acids were found to belong to the benzein series.

2. Those derived from benzoic, salicylic, anisic, gallic and *p*-hydroxy-, *m*- and *p*-nitro-, *m*-bromo- and *p*-chlorobenzoic acids together with some derivatives are described.

3. The dye derived from *p*-hydroxybenzoic acid and melting at 107–108° gives a "homochromo-isomer" melting at 192°.

CALCUTTA, INDIA