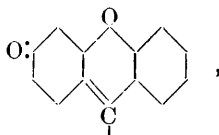


LXXXI.—*Fluorones.*

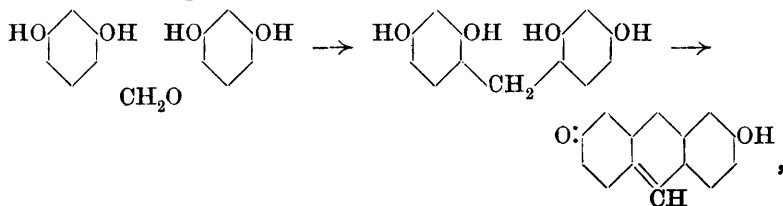
By FRANK GEORGE POPE and HUBERT HOWARD.

So far as we can ascertain, the first use of the term fluorone to describe a certain type of heterocyclic compound was made by Möhlau and Koch (*Ber.*, 1894, **27**, 2887), who designated as "fluorone" the following complex :

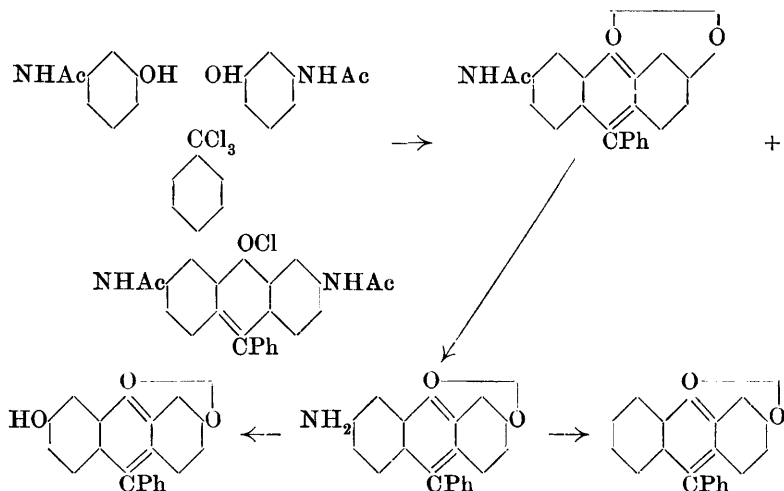


and, since they obtained compounds of this type by the condensation of phenols with aldehydes, the aldehydic grouping appearing in the pyrone ring of the complex, named their compounds according to the aldehyde used as formaldehydefluorone, etc. Kehrman, however, in 1908, considering the group as a whole, gave to the parent substance the name fluorone, and considered all substances derived from it without reference to the particular aldehyde used.

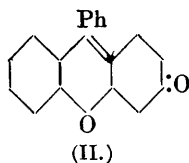
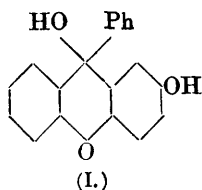
The fluorones of Möhlau and Koch were obtained by the condensation of two molecules of resorcinol with one molecule of an aliphatic aldehyde in the presence of dilute (1 : 5) sulphuric acid, the resulting diphenylmethane derivative being then oxidised to the fluorone by heating with sulphuric acid :



and from their mode of formation they were considered to be compounds of a para-quinonoid type. The hydroxyfluorones obtained in this way were readily soluble in solutions of the alkaline hydroxides, such solutions showing a marked fluorescence. In a similar manner, Weidel and Wenzel (*Monatsh.*, 1900, **21**, 62), Schreier and Wenzel (*ibid.*, 1904, **25**, 311), Liebermann and Lindenbaum (*Ber.*, 1904, **27**, 1171, 2728), by using substituted phloroglucinols and hydroxyquinols in the presence of hydroxyaldehydes, have also prepared many fluorone derivatives. Kehrman (*Ber.*, 1908, **41**, 3440) has obtained phenylfluorone and hydroxyphenylfluorone, starting from acetyl-*m*-aminophenol and benzotrichloride, which, when heated together in nitrobenzene solution at 160°, yield diacetylrosamine chloride and acetylaminophenylfluorone. The acetylaminophenylfluorone is then hydrolysed and the amino-group diazotised, when hydroxyphenylfluorone or phenylfluorone is obtained, accordingly as the diazo-solution is boiled alone or with alcohol, thus:

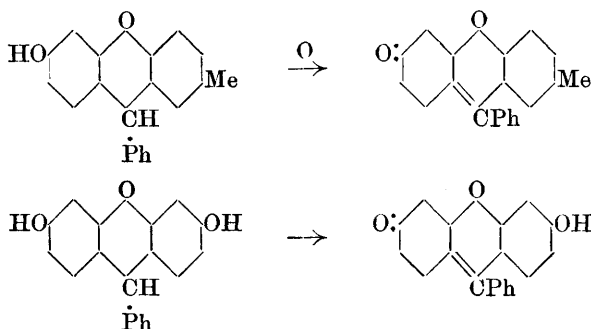


and, in accordance with his well-known views, Kehrman ascribes to these compounds the betaine type of orthoquinonoid structure. This view is combated by Decker (*Ber.*, 1909, **42**, 578), who has tried to prepare the analogue of phenylfluorone from quinolphthalein by hydrolysis of 2-methoxy-9-phenylxanthonium bromide and subsequent neutralisation, but the only product obtained was a colourless carbinol base, namely, 2-hydroxy-9-phenylxanthen-9-ol (I), which shows that there is a fundamental difference between the two series, and the conclusion is drawn that phenylfluorone (II) must have a para-quinonoid structure:



Again, Decker also found that 3-methoxy-9-phenylxanthonium chloride, when heated with hydrochloric acid under pressure, yielded the corresponding hydroxy-compound, which was converted by sodium hydroxide into phenylfluorone, the properties of which bear no resemblance to those of a phenol-betaine, which should be soluble in water.

In the course of this investigation, we have found that the hydroxy-xanthenes obtained by the condensation of dihydroxybenzhydrols with phenols may be oxidised quite readily to fluorones by drawing a slow current of air through their solutions in the alkaline hydroxides, and in this way we have prepared phenylmethylfluorone and 3-hydroxy-9-phenylfluorone, thus :



and it seems to us that since the above phenylmethylfluorone is insoluble in water and also is quite insoluble in solutions of sodium hydroxide, even when boiled, that the betaine formula of Kehrman is untenable, and the compounds in question must be considered as paraquinonoid in structure.

Kehrman is also of the opinion that hydroxyphenylfluorone is identical with Doebner's resorcinolbenzein, $C_{38}H_{30}O_9$, a view which has been denied by H. v. Liebig (*J. pr. Chem.*, 1908, [ii], 78, 534). We are inclined to support Kehrman's views in this matter from a few experiments we have made with resorcinolbenzein as prepared by Cohn from the condensation of resorcinol with benzoic acid in the presence of zinc chloride. A consideration of the formula given by Doebner might suggest that resorcinolbenzein was a hydrated form of hydroxyphenylfluorone, $2(C_{19}H_{12}O_3) \cdot 3H_2O$. We found that Cohn's preparation

gave varying numbers on analysis, and in order to see that the preparation was quite dry, it was heated for many hours at 200°, when it became quite solid after having previously melted at about 150°. Analysis of this product showed a considerable increase in the percentage of carbon, approaching to the value for that of the fluorone. The compound was then heated under reflux with nitrobenzene for some hours, and the solution filtered into light petroleum, when a dark brown, flocculent precipitate was obtained, which was collected, well washed with light petroleum, and dried until quite free from all traces of nitrobenzene :

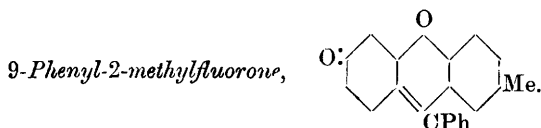
0.0504 gave 0.1445 CO₂ and 0.0158 H₂O. C = 78.19 ; H = 3.48.

C₃₈H₃₀O₉ requires C = 72.38 ; H = 4.76 per cent.

C₁₉H₁₂O₃ „ C = 79.16 ; H = 4.16 „

On these grounds we think that Kehrmann's views are correct, but we hope to return to the subject shortly, since we think that many of the products obtained from resorcinolbenzein can be explained on the same grounds.

EXPERIMENTAL.

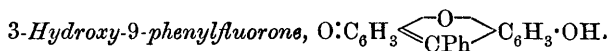


Two grams of 6-hydroxy-9-phenyl-2-methylxanthen were dissolved in an excess of dilute sodium hydroxide solution, and a stream of air was drawn through the liquid for several days. The colour of the solution was gradually discharged until it became of a faint brown shade, and a dark-coloured solid gradually separated. This was collected, washed, dried, and recrystallised from absolute alcohol :

0.1156 gave 0.3550 CO₂ and 0.0520 H₂O. C = 83.75 ; H = 4.99.

C₂₀H₁₄O₂ requires C = 83.91 ; H = 4.89 per cent.

9-Phenyl-2-methylfluorone is an orange-red, crystalline powder, which is only very sparingly soluble in alcohol or chloroform. It is quite insoluble in aqueous alkali hydroxides, and even in dilute solutions of the mineral acids. It dissolves in concentrated sulphuric acid to a dark reddish-brown solution, from which it is reprecipitated by the addition of water. It melts at 201°.



Five grams of 3:6-dihydroxy-9-phenylxanthen were dissolved in an excess of *N*-sodium hydroxide solution, and a stream of air was drawn through the solution for two or three days. The dark-

coloured solution was then diluted with water and acidified with dilute hydrochloric acid, when a dark brown finely-divided precipitate was obtained. This was collected, well washed, and dried, and finally recrystallised from alcohol, from which it separates in dark brown scales possessing a deep blue reflex:

0.1180 gave 0.3418 CO_2 and 0.0436 H_2O . $\text{C} = 79.00$; $\text{H} = 4.10$.

$\text{C}_{19}\text{H}_{12}\text{O}_3$ requires $\text{C} = 79.17$; $\text{H} = 4.17$ per cent.

3-Hydroxy-9-phenylfluorone is a dark brown powder, which is readily soluble in alkali hydroxides, the solution obtained showing a strong green fluorescence. It is soluble in concentrated sulphuric acid, with formation of a brown solution. Since analysis is not quite sufficient to determine the difference between the hydroxyfluorone and the corresponding xanthen, which requires $\text{C} = 78.62$; $\text{H} = 4.83$ per cent., the fluorone was acetylated by heating it with five times its weight of acetic anhydride and its own weight of fused sodium acetate for three hours under reflux. The product was poured into dilute alcohol and warmed on the water-bath for some time in order to remove the excess of anhydride. It was then collected, washed, and dried. For analysis it was dissolved in chloroform and precipitated by light petroleum:

0.1015 gave 0.2836 CO_2 and 0.0390 H_2O . $\text{C} = 76.20$; $\text{H} = 4.27$.

$\text{C}_{21}\text{H}_{14}\text{O}_4$ requires $\text{C} = 76.31$; $\text{H} = 4.27$ per cent.,

whereas the dihydroxyxanthen diacetate requires $\text{C} = 73.80$; $\text{H} = 4.81$ per cent. Thus there seems to be no doubt that the original compound is the fluorone. *3-Acetoxy-9-phenylfluorone* is a dark brown-coloured powder.

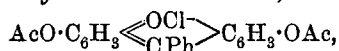
Attempts were made to prepare a hydroxyphenylfluorone hydrochloride, but the product obtained did not give sharp numbers on analysis. The method adopted for the preparation was to dissolve the fluorone in chloroform and saturate the solution with hydrogen chloride, when a dark reddish-brown precipitate was produced. We then modified the method by weighing out a definite quantity in a porcelain boat, which was placed in a piece of glass tubing, and a slow stream of hydrogen chloride was passed over it for several hours and the gain in weight noted:

0.1132 gave 0.1286 hydrochloride.

The ratio $\text{C}_{19}\text{H}_{12}\text{O}_3 \cdot \text{HCl} : \text{C}_{19}\text{H}_{12}\text{O}_3 = 1.127 : 1$.

Actual ratio obtained = 1.136.

3 : 6-Diacetoxy-9-phenylxanthonium chloride,



was prepared by dissolving 2.88 grams of 3-hydroxy-9-phenylfluorone in

chloroform and stirring into the solution 1·57 grams of acetyl chloride. The dark brown precipitate was collected and well washed with chloroform and benzene, and then dried :

0·1162 gave 0·2896 CO_2 and 0·0482 H_2O . $\text{C} = 67·97$; $\text{H} = 4·60$.

$\text{C}_{23}\text{H}_{17}\text{O}_5\text{Cl}$ requires $\text{C} = 67·56$; $\text{H} = 4·16$ per cent.

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