CCXXIII.—*Some Substituted Phenyl Styryl Ketones, with Remarks on the Condensation of Cinnamic Acid with Resorcinol and Pyrogallol.*

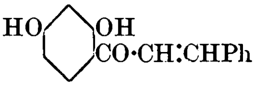
By Thomas Eric Ellison.

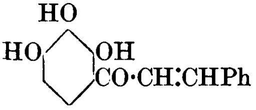
The condensation of benzoic acid with resorcinol in presence of zinc chloride takes place in two stages; 2 : 4-dihydroxybenzophenone is formed first and then, by further heating and participation of a second molecule of resorcinol in the reaction, 3-hydroxy-9-phenylfluorone. Pyrogallol behaves in an analogous fashion to resorcinol.

The behaviour of other simple carboxylic acids with these two phenols depends essentially on the relative velocity of the second stage of the reaction. When this is slow, as, *e.g.*, with acetic acid, the hydroxy-ketone can readily be isolated: when it is rapid, the only products that can be obtained are fluorones or more complex colouring matters In the case of cinnamic acid, the primary condensation products would be hydroxyphenyl styryl ketones (hydroxychalkones); and the formation of chalkones in this way has actually been reported, that of 2 : 4-dihydroxyphenyl styryl ketone (I) from cinnamic acid and resorcinol by Bargellini and Marantonio (*Atti R. Accad. Lincei*, 1908, **17**, ii, 119) and that of 2 : 3 : 4-trihydroxyphenyl styryl ketone (II) from cinnamic acid and pyrogallol by Dutta and Watson (J., 1912, **101**, 1238).

In the hope of being able to extend this method to the synthesis of some of the less accessible chalkones, their work has now been repeated, but the compounds in question were obtained neither by following the details given by the authors nor by any variations of the method, the only substances isolated being more complex colouring matters. To throw more light on the question, the chalkones (I) and (II) have been synthesised by more orthodox methods, and it is found that they are not identical with the substances held to be chalkones by the authors cited. It seems, therefore, that if, in the condensation of cinnamic acid with resorcinol and pyrogallol by means of zinc chloride, chalkones are formed at all, which is very probable, they are so rapidly transformed into more complex products that it is impossible to isolate them.

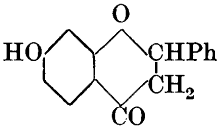
(I.)

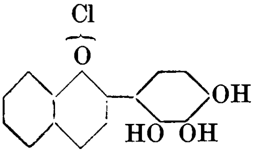




(II.)

(III.)





(IV.)

Resacetophenone and benzaldehyde condense together in alkaline-alcoholic solution to give a mixture of 2 : 4-dihydroxyphenyl styryl ketone (I) and the isomeric 7-hydroxyflavanone (III). It is not uncommon to find chalkone and flavanone being simultaneously formed by this method, and the possibility of the two products being, in this particular case, geometrical isomerides is excluded by the colourless nature of the second substance and the fact that it yields only a monoacetyl derivative. Gallacetophenone and benzaldehyde condense together readily both in acid and in alkaline solution. By boiling with alcoholic hydrochloric acid, they yield benzylidenebisgallacetophenone, $C_6H_5{\cdot}CH[CH_2{\cdot}CO{\cdot}C_6H_2(OH)_3]_2$ (Kostanecki and Blumstein, *Ber.*, 1900, **33**, 1478). The same compound is obtained by saturating a solution of the reagents in glacial acetic acid with dry hydrogen chloride.

Despite the quantitative nature of this reaction, similar compounds cannot be obtained when benzaldehyde is replaced by anisaldehyde, salicylaldehyde, piperonal, or *m*-nitrobenzaldehyde. By the use of alcoholic potash, the required chalkone (II) is obtained in good yield. In order to establish the generality of the last-mentioned method, which does not appear to have been applied hitherto to gallacetophenone, the benzaldehyde was replaced in turn by salicylaldehyde, *m*-hydroxybenzaldehyde, vanillin, and resorcylaldehyde. The last two were found not to condense appreciably with gallacetophenone under the action of alcoholic potash, whereas salicylaldehyde gave a moderate yield of 2 : 3 : 4-trihydroxyphenyl 2-hydroxystyryl ketone,

$$C_6H_2(HO)_3{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH,$$

and *m*-hydroxybenzaldehyde a small amount of 2 : 3 : 4-trihydroxyphenyl 3-hydroxystyryl ketone. Salicylidenegallacetophenone is very slowly converted into 2′ : 3′ : 4′-trihydroxy-2-phenylbenzopyrylium chloride (IV) by the action of anhydrous hydrogen chloride on the suspension in ether; but owing to the small amount of this substance which has so far been isolated, the investigation of it is not yet completed.

EXPERIMENTAL.

2 : 4-*Dihydroxyphenyl Styryl Ketone* (I) and 7-*Hydroxyflavanone* (III).—To a solution of resacetophenone (20 g.) and benzaldehyde (13·3 g.) in methyl alcohol (120 c.c.), potassium hydroxide (40 g. in 40 c.c. of water) was added and the mixture was kept at 65° for 3½ hours and then poured into water. Unchanged benzaldehyde having been extracted with ether, an excess of hydrochloric acid was added, which precipitated a yellow oil (about 12 g.). After 12 hours, the partly solidified oil was carefully treated with glacial acetic acid, and the undissolved solid, consisting of almost pure 7-hydroxyflavanone, was crystallised from toluene. Addition of water to the acetic acid solution precipitated a mixture of the chalkone and flavanone, which were ultimately separated by a tedious fractional crystallisation from toluene, in which the chalkone is the more soluble. 7-*Hydroxyflavanone* crystallises from toluene in colourless needles, m. p. 189° (Found : C, 74·8; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). It is insoluble in water and moderately easily soluble in alcohol or glacial acetic acid. In cold sodium carbonate solution, it gives a colourless solution which turns yellow on boiling. In sodium hydroxide, it at once forms a yellow solution which goes darker on heating owing to the conversion of the flavanone into the chalkone, but the change is never complete.

The flavanone (1 g.) was heated on the water-bath for 3 hours with acetic anhydride (10 c.c.) and anhydrous sodium acetate (5 g.). The *acetyl* derivative thus produced crystallised from 50% alcohol in colourless needles, m. p. 98° (Found : C, 72·0; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

2 : 4-*Dihydroxyphenyl styryl ketone* crystallises from toluene in bright yellow, rectangular prisms, m. p. 133—134° (Found : C, 74·9; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). It is very slightly soluble in boiling water and very soluble in alcohol, glacial acetic acid, and acetone. It forms a deep yellow solution in concentrated sulphuric acid.

2 : 3 : 4-*Trihydroxyphenyl Styryl Ketone* (II).—Gallacetophenone (4·2 g.) and benzaldehyde (2·7 g.) were dissolved in alcohol (4·5 c.c.), and potassium hydroxide (9 g. in 10 c.c. of water) was added. The mixture was kept at 60° for 3 hours and then poured into dilute hydrochloric acid, on which the *chalkone* separated as a brown oil (about 4 g.) which slowly solidified. It was repeatedly crystallised from 75% methyl alcohol, animal charcoal being used to remove a slightly fluorescent, dark impurity, and was thus obtained in orange-yellow prisms containing methyl alcohol of crystallisation. After drying at 110°, it had m. p. 165—166° (Found : C, 70·2; H, 4·9. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%). It forms deep brown solutions in alkali and in concentrated sulphuric acid. It is practically insoluble in water, slightly soluble in benzene and toluene, and very soluble in acetic acid and alcohol.

2 : 3 : 4-*Trihydroxyphenyl 2-Hydroxystyryl Ketone*.—Gallacetophenone (4·2 g.) and salicylaldehyde (3·1 g.), dissolved in alcohol, were treated with potassium hydroxide (10 g. in 10 c.c. of water), and the solution kept at 65° for 3½ hours. Dilute hydrochloric acid was then added which precipitated the *chalkone* (3·3 g.) as a brown oil, which soon solidified. It crystallised from 75% methyl alcohol in long, yellow needles having a light brown colour in bulk. It became almost black at 205° and melted with complete decomposition at 224—225° (Found : C, 65·8; H, 4·4. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%). The chalkone is insoluble in water, benzene, and chloroform, slightly soluble in boiling xylene, and very soluble in acetone and alcohol. It gives dark brown solutions in alkali and in concentrated sulphuric acid, and on heating with concentrated hydrochloric acid it is slowly converted into the pyrylium chloride, but with much decomposition.

2 : 3 : 4-*Trihydroxyphenyl 3-Hydroxystyryl Ketone*.—Gallacetophenone (2·5 g.), *m*-hydroxybenzaldehyde (1·8 g.), potassium hydroxide (5 g. in 5 c.c. of water), and alcohol (40 c.c.) were heated together at 75° for 8 hours. Addition of dilute hydrochloric acid precipitated the *chalkone* (1 g.), which crystallised from 80% methyl alcohol (charcoal) in bright yellow needles, melting at 219—220° to a dark red liquid (Found : C, 66·0; H, 4·7. $C_{15}H_{12}O_5$ requires

C, 66·2; H, 4·4%). It forms a deep brown solution in alkali and a deep orange solution in concentrated sulphuric acid.

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