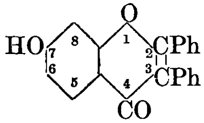
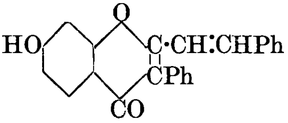
CCCXCII.—*Colloidal Phenoxides. Part I. The Relation between Constitution and Colloidal Properties in Benzo-γ-pyrones.*

By Wilson Baker and Frances May Eastwood.

Certain substituted hydroxy-derivatives of benzo-γ-pyrone (chromone) have been found to give gels of considerable strength when their hot, alkaline solutions (*e.g.*, 1% in slight excess of aqueous sodium hydroxide) are cooled. This was first observed with the sodium salts of 7-hydroxy-2 : 3-diphenylbenzo-γ-pyrone (I) and 7-hydroxy-3-phenyl-2-styrylbenzo-γ-pyrone (II) (Baker and Robinson, J., 1925, **127**, 1981*), and later with 5 : 7-dihydroxy-3-*p*-methoxyphenyl-2-styrylbenzo-γ-pyrone (III) (*idem*, J., 1926, 2713).

(I.)





(II.)

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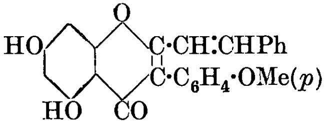
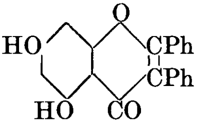
* The substances were here referred to as substituted flavones or *iso*flavones, but for the sake of uniformity they are regarded in this paper as substituted benzo-γ-pyrones.

Some years ago it was suggested to one of us (W. B.) by Dr. F. Fairbrother, of the Victoria University of Manchester, that a fluorescent gel-forming substance would possibly be of use in elucidating the structure of gels, since it might permit of a differentiation between the two phases of the structure, provided that this is not beyond the limits of microscopic resolution. The synthesis and examination of such a compound is the motive underlying this series of papers, and in particular, this paper deals with the relationship between chemical constitution and ability to form gels, describing the synthesis of some benzo-γ-pyrones (a few of which have this property in dilute sodium hydroxide solution), the effect of varying the number and positions of the hydroxyl groups in the " benzo " nucleus, and also the effects caused by altering the substituents in positions 2 and 3. The results may be summarised as follows.

(III.)

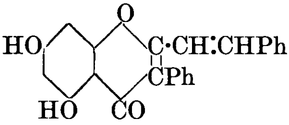


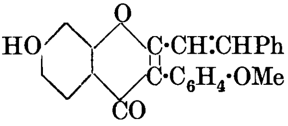


(IV.)

The phloroglucinol derivatives (IV) and (V), corresponding in structure to the resorcinol derivatives (I) and (II), give gels in alkaline solution, as does also the resorcinol derivative (VI), which thus corresponds with its phloroglucinol analogue (III).

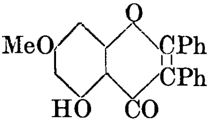
(V.)



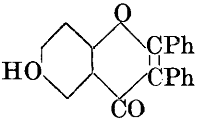


(VI.)

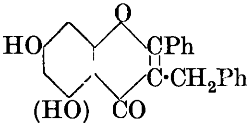
It has been found throughout that the behaviour of corresponding resorcinol and phloroglucinol derivatives towards alkali is identical. This might be expected since the hydroxyl group in position 5, owing probably to the co-ordination of its hydrogen with the oxygen of the neighbouring carbonyl group, possesses such weakly acidic properties that its presence does not confer solubility in aqueous alkalis upon a compound. Thus the 5-hydroxy-compound (VII) is insoluble even in boiling aqueous sodium hydroxide.



(VII.)



(VIII.)



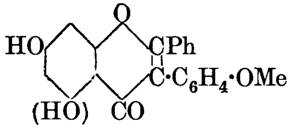
(IX.)

The 6-hydroxy-derivative (VIII), corresponding to the 7-hydroxy-derivative (I), gives no gel, but the alkali salts are very sparingly soluble in water. Monohydroxy-compounds containing the hydroxyl group in position 8 were not available, but it may be noted that

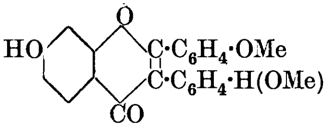
7 : 8-dihydroxy-2 : 3-diphenylbenzo-γ-pyrone (Baker, J., 1925, **127**, 2349) posesses normal phenolic properties.

All the benzo-γ-pyrones which give colloidal phenoxides have aromatic groups in positions 2 and 3. A large number of compounds containing only one aromatic substituent in these positions and hydroxyl groups in position 7, or 5 and 7, are known (flavones, *iso*flavones, and many synthetical alkyl derivatives thereof), but they all behave normally towards alkalis. The substituents in positions 2 and 3 which confer colloidal properties on the phenoxides are phenyl, *p*-methoxyphenyl, and styryl, in certain combinations only. Compounds containing a benzyl group in position 3, *e.g.*, (IX) and its 5-hydroxy-derivative (Baker, *loc. cit.*), yield no gel. Compounds containing a benzyl group in position 2 were not available (see succeeding section).

Neither (X) nor its phloroglucinol analogue (XI) gives a gel in alkaline solution, so that the introduction of the *p*-methoxy-group into the 3-phenyl nucleus inhibits gel formation. This is also seen by comparing (XII) and (XIII), of which only (XII) gives a colloidal phenoxide. This effect of the methoxy-group is not exercised in the cases of (III) and (VI), where a styryl group is present in position 2. Somewhat unexpectedly the 2-veratryl derivative (XIV) gave no gel, but its behaviour towards alkaline solutions is by no means normal (see Experimental).



(X.) and (XI, with OH.)



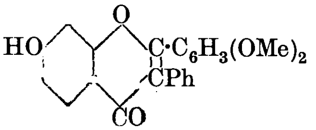
(XII.) and (XIII, with OMe.)

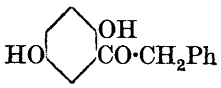
It will be seen that no simple relation exists between the properties of the alkali salts and the constitution of these substances, although a few generalisations may be made. For the formation of a colloidal phenoxide, the following substituents must be present in the benzo-γ-pyrone nucleus: (1) a hydroxyl group in position 7, with or without a further such group in position 5; (2) a phenyl, *p*-methoxyphenyl, or styryl group in position 2 (further substitution in these groups is not necessarily excluded); (3) a phenyl group in position 3, except when a styryl group occupies position 2, in which case a *p*-methoxyphenyl group may replace the phenyl group.

It must be noted that the abnormal properties of the alkali salts of (VIII) and (XIV) indicate that many of these compounds may not differ fundamentally to so great an extent as a consideration of their colloidal properties alone would seem to show, and hence such substances of closely allied constitution cannot perhaps be expected to possess similar colloidal properties.

Preparation of the Benzo-γ-pyrones, etc.—The benzo-γ-pyrones were prepared from *o*-hydroxyphenyl benzyl ketones by fusion with a mixture of the anhydride and sodium salt of an aromatic acid. The necessary ketones were prepared by means of the Hoesch reaction with the exception of 2 : 5-*dihydroxyphenyl benzyl ketone* (XV) required for the synthesis of 6-*hydroxy*-2 : 3-*diphenylbenzo-γ-pyrone* (VIII). This ketone, m. p. 109·5°, was obtained by the condensation of phenylacetyl chloride with quinol dimethyl ether and subsequent demethylation of the product. A compound described as having this structure was isolated by Finzi (*Monatsh.*, 1905, **26**, 1135) from the product of interaction of quinol and phenylacetic acid in presence of zinc chloride, and of quinol and phenylacetyl chloride in presence of aluminium chloride. We have repeated both these reactions many times and under various conditions, but the only isolable phenolic product has been unchanged quinol, m. p. 170°. Since Finzi's product was stated to melt at 170°, and its description and recorded properties (excepting the elementary analysis) agree exactly with those of quinol, we are of the opinion that it was actually quinol.

(XIV.)

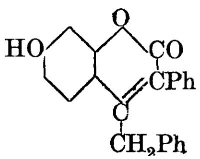


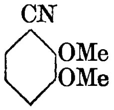


(XV.)

In attempts to prepare benzo-γ-pyrones with a benzyl group in position 2, 2 : 4-dihydroxyphenyl benzyl ketone and 2 : 4-dihydroxyphenyl β-phenylethyl ketone were heated with phenylacetic anhydride and sodium phenylacetate. In the first case the product proved to be 7-*hydroxy*-3-*phenyl*-4-*benzylcoumarin* (XVI), and in the second case the analogous 7-*hydroxy*-3 : 4-*dibenzylcoumarin*. Both substances gave powerfully fluorescent solutions in all solvents, and even in the form of their methyl ethers were devoid of basic oxonium properties. The methyl ether of (XVI) readily dissolved to a yellow solution in alcoholic potassium hydroxide owing to rupture of the lactone ring. The formation of these coumarins is undoubtedly connected with the reactivity of the methylene group in phenylacetic acid. Acids with less reactive methylene groups, such as acetic or β-phenylpropionic acid (Robinson and Shinoda, J., 1925, **127**, 1976), condense normally to give benzo-γ-pyrones.

(XVI.)





(XVII.)

The ketonic intermediates for the preparation of 8-hydroxybenzo-γ-pyrones could not be produced. Magnesium benzyl cyanide would not react with 2 : 3-dimethoxybenzaldehyde nor with 2 : 3-*dimethoxybenzonitrile* (XVII). This nitrile was prepared by dehydrating 2 : 3-dimethoxybenzaldoxime with acetic anhydride and sodium acetate. A further attempt to prepare an 8-hydroxy-derivative was made by treating α-phenylacetoacetic ester with guaiacol in presence of phosphoric anhydride with the intention of producing 8-methoxy-3-phenyl-2-methylbenzo-γ-pyrone, the methyl group of which could subsequently be condensed with benzaldehyde (compare Heilbron, Barnes, and Morton, J., 1923, **123**, 2559), but the reaction gave only a trace of a *substance*, $C_{18}H_{16}O_2$, m. p. 203°. This formula may be derived by the condensation of 2 mols. of α-phenylacetoacetic ester with loss of 2 mols. of alcohol and 1 mol. of carbon dioxide, but the substance could not be produced directly from the ester and phosphoric anhydride, and its constitution remains undecided.

EXPERIMENTAL.

7-*Hydroxy*-3-*phenyl*-2-*styrylbenzo*-γ-*pyrone* (II).—7-Cinnamoyloxy-3-phenyl-2-styrylbenzo-γ-pyrone (1 g.; Baker and Robinson, J., 1925, **127**, 1985), suspended in alcohol (10 c.c.), was heated for 5 minutes with potassium hydroxide (0·5 g.) dissolved in a little water. The solution was diluted with water (10 c.c.), and the phenolic *compound* precipitated by saturation with carbon dioxide. It crystallises from alcohol, in which it is sparingly soluble, in very pale yellow needles, m. p. 298° (slight decomp.) (Found: C, 81·1; H, 4·7. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), and dissolves in hot dilute sodium hydroxide to a bright yellow solution which sets to a gel on cooling, and slowly deposits very fine, hair-like growths. The solution in concentrated sulphuric acid is bright lemon-yellow with a greenish-blue fluorescence, but the colour fades considerably after several hours.

5 : 7-*Dihydroxy*-2 : 3-*diphenylbenzo*-γ-*pyrone* (IV).—Anhydrous 2 : 4 : 6-trihydroxyphenyl benzyl ketone (20 g.; Chapman and Stephen, J., 1923, **123**, 404), benzoic anhydride (120 g.), and sodium benzoate (10 g.) were stirred and heated at 180—190° for 10 hours. The product was hydrolysed by heating with alcohol (200 c.c.) and a solution of potassium hydroxide (60 g.) in water (120 c.c.) for ½ hour, and after addition of water (400 c.c.) the phenolic *compound* was isolated as above. It was crystallised twice from glacial acetic acid, in which it is somewhat sparingly soluble, and separated in pale yellow, almost rectangular prisms, m. p. 252° (Found: C, 76·2; H, 4.4. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). The substance dissolves in dilute sodium hydroxide only on being heated, and gives

a pale yellow solution, which sets to a clear, rigid gel on cooling. The solution in concentrated sulphuric acid is pale yellow, and exhibits a very weak bluish fluorescence.

5-*Hydroxy*-7-*methoxy*-2 : 3-*diphenylbenzo*-γ-*pyrone* (VII).—The substance (IV) was methylated below 50° in 5% aqueous potassium hydroxide with methyl sulphate. The solid product proved to be a mixture of the mono- and the di-methyl ether, from which the former was isolated by repeated crystallisation from glacial acetic acid, separating in thick, very pale yellow, oblong, rectangular plates, m. p. 193—194° (Found: C, 76·9; H, 5·0. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). The *pyrone* develops an intense violet-red colour with ferric chloride in alcoholic solution. It is insoluble in cold or hot aqueous sodium hydroxide, but gives yellow solutions of the alkali salt in alcoholic or acetone solutions of sodium hydroxide.

5 : 7-*Dihydroxy*-3-*phenyl*-2-*styrylbenzo*-γ-*pyrone* (V).—This compound was prepared from 2 : 4 : 6-trihydroxyphenyl benzyl ketone (10 g.) by the action of cinnamic anhydride and sodium cinnamate in the manner described for the preparation of 5 : 7-dihydroxy-3-*p*-methoxyphenyl-2-styrylbenzo-γ-pyrone (III) (Baker and Robinson, J., 1926, 2718). The intermediate product, 5-*hydroxy*-7-*cinnamoyloxy*-3-*phenyl*-2-*styrylbenzo*-γ-*pyrone*, crystallised from glacial acetic acid (1 l.) in bright yellow, tiny, pointed needles, m. p. 232° (Found, in material heated to 200°: C, 79·0; H, 4·5. $C_{32}H_{22}O_5$ requires C, 79·0; H, 4·5%). The substance retains a small amount of acetic acid with great tenacity. The position of the cinnamoyloxy-group is inferred from the insolubility of the substance in aqueous sodium hydroxide and from the weak greenish-brown colour developed by the addition of ferric chloride to its alcoholic solution. This latter reaction is very weak owing to the sparing solubility of the substance in alcohol.

5 : 7-*Dihydroxy*-3-*phenyl*-2-*styrylbenzo*-γ-*pyrone*, after two recrystallisations from glacial acetic acid, formed tiny, yellow, flat, rhombic prisms, m. p. 281° (slight decomp.) (Found, in material dried at 240° in a vacuum: C, 77·2; H, 4·7. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%). This substance also shows a great tendency to retain acetic acid. The orange-yellow solution in hot, dilute sodium hydroxide sets to a gel on cooling. The solution in concentrated sulphuric acid is bright yellow and exhibits a weak green fluorescence.

2 : 4-*Dihydroxyphenyl* p-*Methoxybenzyl Ketone*.—*p*-Methoxyphenylacetonitrile (23 g.; prepared from anisaldehyde in the manner described for the preparation of 3 : 4 : 5-trimethoxyphenylacetonitrile, Baker and Robinson, this vol., 157) and resorcinol (25 g.) were dissolved in dry ether (100 c.c.), powdered zinc chloride (2 g.)

was added, and the solution saturated with hydrogen chloride at 0°. After hydrolysis of the ketimine by heating with water for 1 hour, the ketone was extracted with chloroform, the solution washed and then shaken with dilute aqueous sodium hyroxide. The alkaline layer on acidification yielded the solid *ketone*, which crystallises from dilute alcohol or chloroform in prismatic needles, m. p. 159° (Found: C, 69·5; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·7; H, 5·4%), and dissolves in alkaline solutions with a pale yellow colour; its alcoholic solution develops a red colour with ferric chloride.

*7-Hydroxy-3-*p*-methoxyphenyl-2-styrylbenzo-γ-pyrone* (VI).—This was prepared from 2 : 4-dihydroxyphenyl *p*-methoxybenzyl ketone as in the case of the analogous compound (V). The intermediate *7-cinnamoyloxy-3-*p*-methoxyphenyl-2-styrylbenzo-γ-pyrone* crystallises from glacial acetic acid or ethyl acetate in tiny, pale yellow, pointed prisms, m. p. 221° (Found: C, 78·7; H, 5·2. $C_{33}H_{24}O_5$ requires C, 79·2; H, 4·8%). The *pyrone* crystallises from a large volume of alcohol in tiny yellow needles, m. p. 304° (Found: C, 78·0; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·8%). It does not dissolve in cold, aqueous alkaline solutions, but dissolves on heating to a yellow solution which sets to a gel on cooling. The bright yellow solution in concentrated sulphuric acid shows a green fluorescence in a source of ultra-violet light.

*7-Hydroxy-2-phenyl-3-*p*-methoxyphenylbenzo-γ-pyrone* (X).—2 : 4-Dihydroxyphenyl *p*-methoxybenzyl ketone (5 g.), sodium benzoate (6 g.), and benzoic anhydride (60 g.) were stirred and heated at 180—190° for 7 hours, then hydrolysed by 15 minutes' heating with potassium hydroxide (35 g.) dissolved in alcohol (250 c.c.) and water (75 c.c.); the phenolic *pyrone*, precipitated by saturating the diluted solution with carbon dioxide, crystallised from alcohol in small, colourless prisms, m. p. 264° (Found: C, 76·7; H, 4·8. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·8%). It dissolves in aqueous alkalis to give yellow solutions which show no tendency to form gels. The pale yellow solution in concentrated sulphuric acid is devoid of fluorescence. The intermediate 7-benzoyloxy-derivative has m. p. 193°.

5 : *7-Dihydroxy-2-phenyl-3-*p*-methoxyphenylbenzo-γ-pyrone* (XI).—This *compound* was prepared from 2 : 4 : 6-trihydroxyphenyl *p*-methoxybenzyl ketone (Baker and Robinson, J., 1926, 2717) by the same method as compound (IV). It crystallises from alcohol in pale yellow needles, m. p. 230—231° (Found: C, 72·9; H, 4·7. $C_{22}H_{16}O_5$ requires C, 73·3; H, 4·5%). The properties of this substance are similar to those of the corresponding resorcinol derivative (X). The acetyl derivative separates from methyl alcohol in colourless, silky needles, m. p. 196—197°.

7-*Hydroxy*-3-*phenyl*-2-p-*methoxyphenylbenzo*-γ-*pyrone* (XII).—2 : 4-Dihydroxyphenyl benzyl ketone (2 g.), anisic anhydride (10 g.), and anhydrous sodium anisate (2 g.) were stirred and heated at 180° for 6 hours. The product was hydrolysed in the usual way with aqueous-alcoholic potassium hydroxide, and the phenolic *compound* was isolated by means of carbon dioxide. It crystallises from alcohol in faintly yellow, prismatic needles, m. p. 288° (Found : C, 76·4; H, 4·9. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%), and in concentrated sulphuric acid gives a pale yellow solution which exhibits a weak blue fluorescence. It is soluble in hot dilute sodium hydroxide, and the pale yellow solution sets to a gel on cooling.

7-*Hydroxy*-2 : 3-*di*-p-*methoxyphenylbenzo*-γ-*pyrone* (XIII).—2 : 4-Dihydroxyphenyl *p*-methoxybenzyl ketone (2·5 g.) was heated with sodium anisate (3 g.) and anisic anhydride (17 g.) at 180° for 6 hours. The product was powdered and hydrolysed by heating with potassium hydroxide (8 g.) in water (30 c.c.) and alcohol (100 c.c.) for 10 minutes, and the phenolic substance isolated in the usual way and crystallised from alcohol. The *compound* is dimorphous, and separates in small, blunt-ended prismatic needles or occasionally in compact bi-pyramids, both forms having m. p. 271—272° (Found : C, 73·8; H, 4·9. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%); it is slightly soluble in dilute, aqueous sodium hydroxide, and shows no sign of gel formation. The yellow solution in concentrated sulphuric acid is without fluorescence. No coloration is developed by the addition of ferric chloride to its alcoholic solution.

7-*Hydroxy*-3-*phenyl*-2-(3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone* (XIV).—To obtain satisfactory yields of this compound the conditions must be carefully controlled. A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (40 g.) and veratric anhydride (136 g.; Allan and Robinson, J., 1926, 2334, method A) was stirred and heated at 190° for 3 hours. Then, during 12 hours, powdered sodium veratrate (40 g.) was slowly introduced, the temperature being finally taken to 200°. The resin-like product was powdered under water, shaken with much dilute sodium carbonate solution, filtered, and washed. The damp powder was heated with alcohol (300 c.c.) and a solution of potassium hydroxide (40 g.) in water (40 c.c.) for ½ hour, water (300 c.c.) was then added, and the phenolic product precipitated by saturation with carbon dioxide (yield, 23 g.). The *substance* crystallises from methyl alcohol in colourless, prismatic needles, m. p. 240° (Found : C, 73·8; H, 5·1. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%); the properties of its alkali salts are remarkable. When the crystals are covered with 8% sodium hydroxide, they appear to melt to a yellow oil, which dissolves on the addition of a considerable volume of water or on heating the liquid. In the latter case the yellow, oily salt separates on cooling. When it is heated with 50% sodium hydroxide, an insoluble yellow oil is produced which sets hard on cooling, and although this is insoluble in the concentrated alkali, it dissolves in a large volume of water to a yellow solution, and is therefore the alkali salt. The basic (oxonium) properties of this compound and its methyl ether (below) are marked: both dissolve to bright yellow solutions in concentrated hydrochloric acid which are decolorised and precipitated on dilution. The basicity of the substituted benzo-γ-pyrones increases with introduction of methoxyl groups. Thus 7-hydroxy-2 : 3-diphenylbenzo-γ-pyrone (I) is insoluble in concentrated hydrochloric acid even on heating, whilst 7-hydroxy-3-phenyl-2-*p*-methoxyphenylbenzo-γ-pyrone (XII) scarcely dissolves giving only very pale yellow solutions.

7-*Methoxy*-3-*phenyl*-2-(3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone*.—The methylation of (XIV) with methyl sulphate gave poor yields in aqueous or alcoholic solutions, but good yields were obtained with acetone as solvent. The compound (XIV) (23 g.) and acetone (200 c.c.) were vigorously shaken, and methyl sulphate (100 c.c.) and excess of 50% aqueous potassium hydroxide slowly added alternately and in small portions. After ½ hour's heating on the steam-bath, water was added, and the methyl *ether* collected and washed (yield 23·5 g.). It crystallises from methyl alcohol in colourless, thick, flat prisms, m. p. 181° (Found: C, 74·2; H, 5·6. $C_{24}H_{20}O_5$ requires C, 74·3; H, 5·2%).

2 : 5-*Dihydroxyphenyl Benzyl Ketone* (XV).—2 : 5-Dimethoxyphenyl benzyl ketone (Kauffmann, *Annalen*, 1905, **344**, 65) was demethylated by heating on the water-bath for 2 hours with a mixture of equal volumes of hydriodic acid (*d* 1·7) and glacial acetic acid. Addition of water caused the separation of a solid which crystallised from carbon tetrachloride in pale lemon-yellow, rhombic prisms, m. p. 109·5° (Found: C, 73·8; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%). 2 : 5-*Dihydroxyphenyl benzyl ketone* is readily soluble in alcohol, and the solution develops a green colour on the addition of ferric chloride. Its solutions in alkali are bright yellow, and when treated with methyl sulphate, they regenerate the dimethyl ether, m. p. 48°.

6-*Hydroxy*-2 : 3-*diphenylbenzo*-γ-*pyrone* (VIII).—The ketone (XV) (2 g.) was fused with benzoic anhydride (20 g.) and anhydrous sodium benzoate (2 g.) at 180—190° for 8 hours. The product was hydrolysed by heating with alcohol (25 c.c.) and a solution of potassium hydroxide (20 g.) in water (25 c.c.) for 15 minutes, after which water (50 c.c.) was added and the phenolic product precipitated by saturation with carbon dioxide. It crystallised from methyl alcohol in colourless, prismatic needles, m. p. 258—260° (slight decomp.)

(Found: C, 80·3; H, 4·5. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). 6-*Hydroxy*-2 : 3-*diphenylbenzo*-γ-*pyrone* gives no characteristic colour on the addition of ferric chloride to its alcoholic solution. The pale yellow solution in concentrated sulphuric acid exhibits a weak greenish-blue fluorescence in ultra-violet light. It is almost insoluble in cold aqueous sodium hydroxide solution, but dissolves on warming, and on cooling, the sodium salt separates in glistening bright yellow laminæ. This salt dissolves on the addition of a large volume of water.

7-*Hydroxy*-3-*phenyl*-4-*benzylcoumarin* (XVI).—Phenylacetic anhydride (20 g.; prepared by boiling the acid with 2½ times its weight of acetic anhydride for 8 hours and removing the acetic acid and excess of acetic anhydride under diminished pressure) was mixed with 2 : 4-dihydroxyphenyl benzyl ketone (4 g.) and sodium phenylacetate (5 g.) and heated at 180° for 8 hours. After hydrolysis, the *coumarin* was isolated in the usual manner, and crystallised from alcohol in colourless, compact, bi-pyramids, m. p. 232° (Found: C, 80·4; H, 5·3. $C_{22}H_{16}O_3$ requires C, 80·7; H, 5·3%). It dissolves in concentrated sulphuric acid and in dilute, aqueous sodium hydroxide to almost colourless solutions, which exhibit marked blue fluorescence. The solution in alcoholic potassium hydroxide is pale yellow with a strong greenish-blue fluorescence. The *methyl ether*, prepared by the action of methyl sulphate and potassium hydroxide in acetone solution, crystallised from alcohol in colourless, thick prisms, m. p. 183—184° (Found: C, 80·4; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%); it dissolves readily in alcoholic potassium hydroxide to a yellow solution, and is thus sharply distinguished from a benzo-γ-pyrone. Further, it exhibits no basic properties towards concentrated hydrochloric acid as do the methylated benzo-γ-pyrones.

Attempts were made to synthesise (XVI), (i) by the condensation of $\alpha\gamma$-diphenylacetoacetic ester (Volhard, *Annalen*, 1897, **296**, 16) with a very large excess of resorcinol in the presence of concentrated sulphuric acid, but the reaction gave only 1 : 3-dihydroxy-2-phenylnaphthalene (*idem, ibid.*; compare Jacobson and Ghosh, J., 1915, **107**, 966), and (ii) by heating a mixture of 2 : 4-dihydroxyphenyl benzyl ketone, sodium phenylacetate, and acetic anhydride (compare Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 121; Bargellini, *Gazzetta*, 1927, **57**, 459; Baker, this vol., p. 1599). It was found, however, that the sodium phenylacetate did not take part in the reaction, and that the only product was 7-acetoxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 162° (Baker and Robinson, J., 1925, **127**, 1984).

7-*Hydroxy*-3 : 4-*dibenzylcoumarin*.—A mixture of benzylresacetophenone (4 g.; Baker, J., 1925, **127**, 2355), phenylacetic anhydride (20 g.), and sodium phenylacetate (4 g.) was heated at 160° for 8 hours. The product was isolated in the usual way and separated from methyl alcohol in colourless, thick prisms, m. p. 220° (Found: C, 80·5; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%); it is probably dimorphous, since the mother liquors deposited a small quantity of long needles, m. p. 210°, and a mixture of the two products melted at 217°. 7-*Hydroxy*-3 : 4-*dibenzylcoumarin* dissolves in concentrated sulphuric acid to an almost colourless solution with a strong blue fluorescence. The alkaline solutions exhibit a faint blue fluorescence, whilst the solution in alcoholic potassium hydroxide is light yellow with a marked greenish-blue fluorescence. The *methyl ether*, prepared as in the preceding case, crystallises from alcohol in silky, prismatic needles, m. p. 144° (Found: C, 80·9; H, 5·7. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·7%); it neither reacts with warm alcoholic potassium hydroxide, nor shows basic properties. The hydroxycoumarin could not be synthesised by boiling a mixture of 2 : 4-dihydroxyphenyl benzyl ketone, sodium β-phenylpropionate, and acetic anhydride.

2 : 3-*Dimethoxybenzonitrile* (XVII).—2 : 3-Dimethoxybenzaldoxime (10 g.; Noelting, *Ann. Chim. Phys.*, 1910, **19**, 502) was boiled for 3 hours with acetic anhydride (40 c.c.) and anhydrous sodium acetate (10 g.). Water was then added, and after being shaken and cooled in ice, the oily product solidified. The *nitrile* crystallises from light petroleum (b. p. 40—60°) in colourless, flat, highly refracting prisms, m. p. 47° (Found: N, 8·4. $C_9H_9O_2N$ requires N, 8·6%); it would not condense with magnesium benzyl chloride.

Condensation of Guaiacol with α-Phenylacetoacetic Ester.—A stirred mixture of guaiacol (12 g.), α-phenylacetoacetic ester (10 g.; Beckh, *Ber.*, 1898, **31**, 3160), and xylene (10 c.c.) was heated to 120°, and phosphoric anhydride (40 g.) slowly introduced. Heating was continued for 2 hours and the temperature was finally raised to 140°. The product was distilled in steam and the dark oil dissolved in a warm mixture of benzene and ethyl acetate. The solution was shaken with excess of aqueous sodium hydroxide, dried, boiled with charcoal, and filtered, yielding a small amount of a semi-solid material. After being pressed on porous earthenware, the *substance* was twice crystallised from methyl alcohol and obtained in colourless, rectangular plates (0·3 g.), m. p. 203° (Found: C, 82·7; H, 5·8. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

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