

SOME ANALOGUES OF PHTHALEIN DYES FROM SUCCINIC AND MALEIC ACIDS

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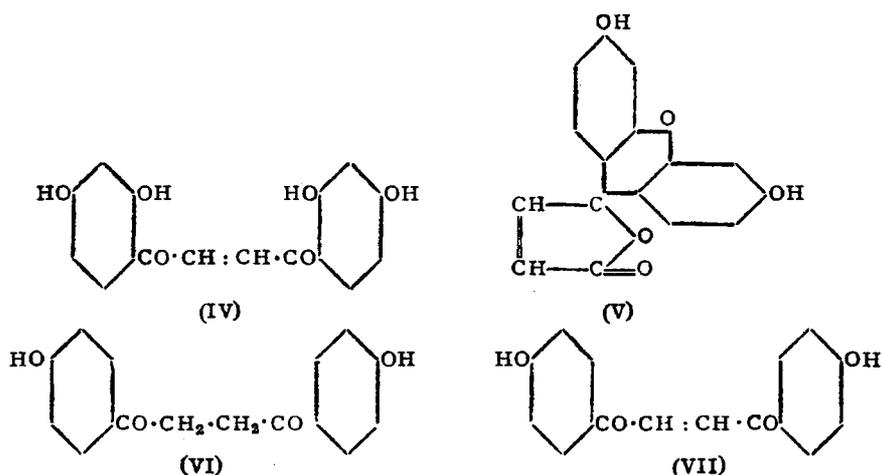
BESIDES their use as dyestuffs, members of the phthalein group have found other uses also. For example, tetraiodofluorescein, known as erythrosin is used as a photographic dye and also as colouring matter for foodstuffs. Tetraiodophenolphthalein has found use as a skiagraphic chemical. Considerable interest has been shown in the mercury compounds derived from these for employment as antiseptics, the most important being 'Mercurochrome'. Analogues of phthaleins derived from succinic and maleic acids have the advantage of smaller molecular weights. Consequently, higher percentages of halogens and mercury could be introduced into them. With this end in view, the preparation of succineins and maleins and their substitution products have now been investigated.

Resorcinol-succinein (I) was made earlier by Biggs and Pope¹ using succinic anhydride, resorcinol and 73% sulphuric acid and they gave its melting point as 234° (decomp.). The method does not seem to give consistent yields and, therefore, we have employed zinc chloride as the condensing agent instead, using a temperature of 170–80°. Under these conditions, it is possible to substitute succinic acid for its anhydride obtaining the same results. The succinein has been obtained in a yield of about 60% and it melts with decomposition at 254–56°.

The dibromo- and tetrabromo-derivatives of the above succinein have been reported already in the literature.¹ By modifying the method of preparation, purer products have now been prepared. Further, the tetraiodo-compound has been newly made, as also the mercuration product.

In the above preparation of resorcinol-succinein, a pale yellow by-product, insoluble in 5% hydrochloric acid (m.p. 310–12°) has been isolated in a low yield. Its composition and properties agree with the diketone constitution, 2:4:2':4'-tetrahydroxy-dibenzoyl-ethane (II). It forms a tetra-acetate, tetramethyl and ethyl ethers, and derivatives with phenylhydrazine and dinitrophenylhydrazine. Though it dissolves in hot aqueous sodium carbonate, its acetate does not dissolve in dilute aqueous

and reactions corresponded with the diketone structure, 2:4:2':4'-tetrahydroxy-dibenzoyl-ethylene (IV). The more soluble fraction had a much deeper colour and exhibited marked fluorescence and all the properties of resorcinol-malein (V). It is, therefore, clear that in this condensation also, two products are formed, the malein in poor yield and the diketone as the major product. The malein gives the bromo-, iodo- and mercuri-derivatives. The use of zinc chloride as the condensing agent for the combination of maleic anhydride or acid and resorcinol is a disadvantage since it gives rise to resinification and the yields and purity of the products suffer.



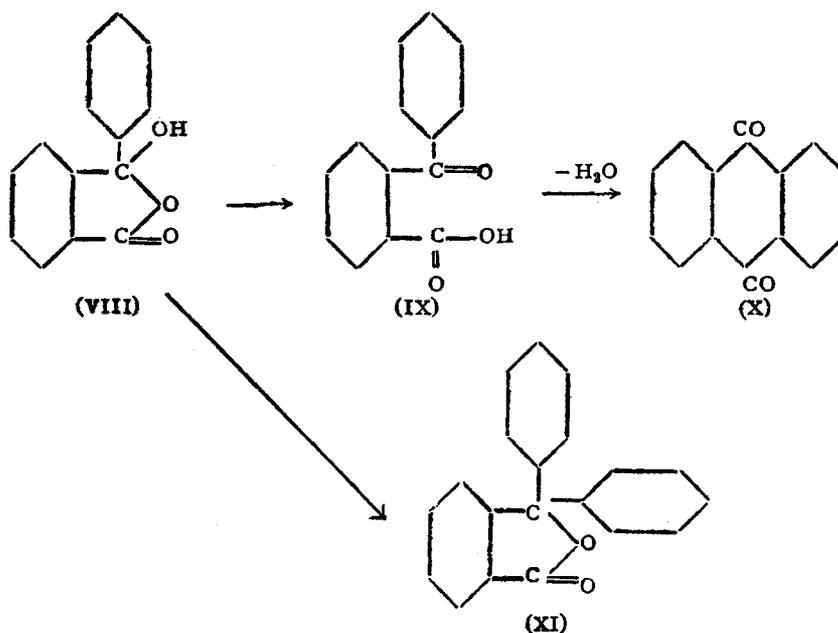
The condensation of phenol with succinic anhydride or acid does not appear to have been investigated before. The use of sulphuric acid as the condensing agent at 120° is not successful. But with zinc chloride, a small yield of a crystalline product (diketone, VI) could be obtained, the major portion being uncrystallisable resinous matter. Higher temperature, say 150°, causes more resinification.

The condensation of phenol and maleic acid was carried out by Dass and Tewari⁴ in the presence of concentrated sulphuric acid at 125–35°. They described it as a brown powder blackening at 175° and melting at 195°. A repetition of the reaction showed that the yield was very poor and the product impure. By employing zinc chloride as the condensing agent, a colourless crystalline substance (m.p. 300° with decomposition) is obtained as the main product; it has the molecular composition C₁₆H₁₂O₄ and gives no colour with alcoholic ferric chloride indicating that the hydroxyl groups are para to the carbonyl. It does not give any prominent colour with sodium hydroxide, though the condensation product in an impure condition produces an appreciable purple colour with alkali. Obviously, the main pro-

duct is the diketone (VII) and only very minor amounts of phenol-malein are formed.

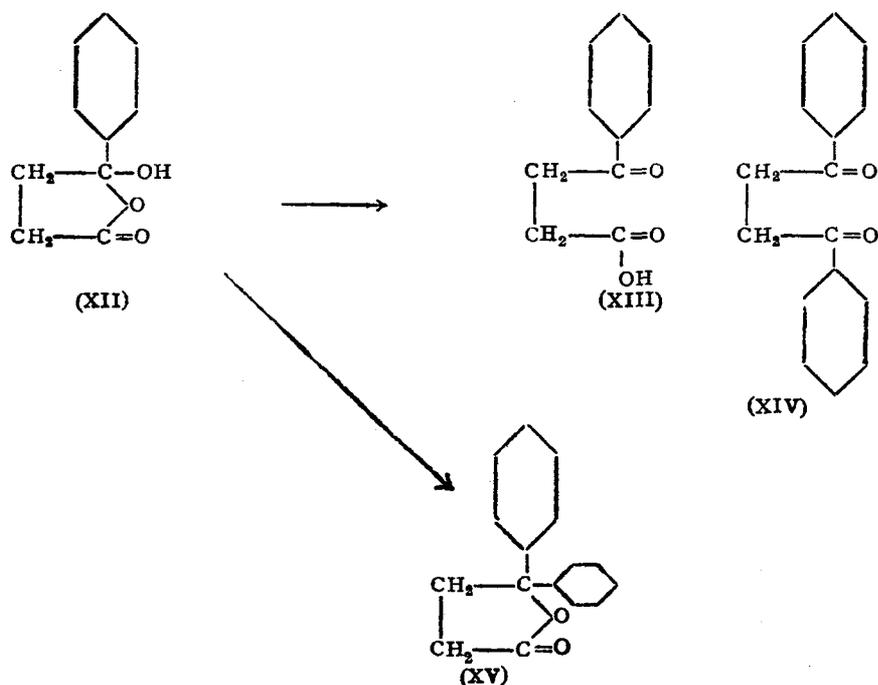
The results obtained during the course of this work could be summed up as follows. Resorcinol condenses with succinic anhydride to yield the succinein as the main product and the diketone is obtained as a small by-product. Orcinol also gives a good yield of the succinein. These could be used conveniently for the preparation of halogen and mercury substituted derivatives. The other condensations have not been successful from this point of view. Resorcinol itself gives only a poor yield of the malein, the major condensation product being the diketone. With regard to phenol, it does not give any isolable quantity of succinein or malein and only diketones could be isolated by condensations with succinic anhydride and maleic anhydride.

There seems to be a number of possible ways in which phthalic, succinic and maleic anhydrides can condense with phenols and related aromatic compounds depending upon the proportions of the reactants, condensing agent and other conditions. All these have not been realised with each substance. Representatives of several of the possible modes of combination are now available. With phthalic anhydride, the phthaleins are well known; next comes the formation of the ketonic acids as represented by benzoyl benzoic acid, and the diketone type found in the anthraquinones.



The formation of alizarin from catechol and phthalic anhydride is a well-known instance. Regarding the details of the reactions, the suggestion of von Braun,² *et al.*, that the initial stage involves attack of a phenol unit on one of the carbonyl groups of the anhydride as shown in (VIII) and (XII) seems to be quite acceptable. The later reactions could be represented as below.

In the case of succinic anhydride, besides the succineins (XV), the ketonic acids (XIII) and the diketones (XIV) are more easily obtained; two phenol units are involved in the formation of the diketones (XIV). Obviously, maleic acid and anhydride show little tendency to form maleins and readily yield diketones. With the aliphatic anhydrides, ring diketones of type (X) have not so far been obtained.



EXPERIMENTAL

Condensation of Resorcinol with succinic acid or anhydride.—

An intimate mixture of resorcinol (10.0 g.) and succinic acid (5.0 g.) was heated at 170° for ½ hour and freshly fused and powdered zinc chloride (0.5 g.) added with stirring. The heating was continued for another 3 hours, the temperature not exceeding 180°. After cooling, the reaction product was treated with acetone (25 c.c.), heated to boiling on a water-bath and

cooled; the solid product that had separated out was filtered and the residue washed with some more acetone (10 c.c.). The acetone washings were marked (W). The required succinein (A) was then separated from the residue by boiling repeatedly with 5% hydrochloric acid in which it dissolved leaving an insoluble pale yellow substance (B).

Component (A): Resorcinol Succinein (I).—

This was purified by crystallisation from 5% hydrochloric acid twice when it appeared as glistening dark crimson rectangular tablets with a blue reflex melting with decomposition at 254–56° (*cf.*, Biggs and Pope¹, 234°). Yield: 5.5 g. (Found: C, 56.6; H, 5.0; loss on drying *in vacuo* at 150–160° for 5 hours 15.6; C₁₈H₁₂O₅, 3H₂O requires C, 56.8; H, 5.3 and loss on drying 16.0%). It was easily soluble in acetone, sparingly soluble in alcohol, and insoluble in petroleum ether. In alkali it formed a deep red solution with a bright green fluorescence resembling that of resorcinol-phthalein. With alcoholic ferric chloride it gave a dark brown colour.

The acetone washings (W), on concentration, gave a highly viscous liquid which slowly solidified during the course of a few days. When extracted with boiling 5% hydrochloric acid it gave some more of the succinein (yield: 1.2 g.) leaving an uncrystallisable resin behind.

The same results were obtained when succinic anhydride was used instead of the acid for the above condensation. The following exploratory experiments were carried out. They are described here in brief.

(1) Resorcinol, succinic anhydride and 73% sulphuric acid were heated together at the boiling temperature according to the method of Biggs and Pope.¹ The crude product obtained was nearly theoretical in yield, but on purification using 5% hydrochloric acid, the succinein was obtained only in 20% yields. Even then it melted only at 234° and was difficult to purify further. The insoluble residue was considerable in quantity and gave strong green fluorescence in alkali solutions. But no more of the pure succinein could be extracted from it.

(2) Resorcinol, succinic acid and zinc chloride heated at 140° did not yield any appreciable amount of the succinein, the starting materials being almost completely recovered.

(3) Resorcinol, succinic acid and zinc chloride were heated together at 200°. There was considerable resinification, the yield of the succinein coming down to 10%.

(4) If instead of adding the zinc chloride to the melt of resorcinol and succinic acid kept at 170°, it was added at the laboratory temperature itself at the beginning and the reaction carried out by heating to 170–80°, the yield of the succinein was only 20% of the theoretical.

The yield of the succinein and the purity of the sample depended largely on the quality of zinc chloride that was employed and only salt of good quality should be used under the conditions described.

Tetrabromo-resorcinol-succinein.—

Resorcinol-succinein (0.5 g.) dissolved in glacial acetic acid (10 c.c.) was treated with cooling under the tap with excess of bromine in the same solvent. The solution immediately deposited a shining deep red crystalline powder. It was filtered and washed free from the mother liquor with glacial acetic acid. It appeared as rhombohedral plates under the microscope. It was sparingly soluble in glacial acetic acid and soluble in aqueous alkali, the solution giving a weak green fluorescence. It decomposed above 300° (Biggs and Pope¹, 250° d). Yield, almost quantitative. (Found: Br, 53.0; C₁₆H₈O₅Br₄ requires Br., 53.3%).

Dibromo-resorcinol-succinein.—

Resorcinol-succinein (0.5 g.) was dissolved in glacial acetic acid and treated with bromine (1.2 g.) in the same solvent. The solution on dilution with water precipitated the dibromo-compound. It was filtered washed with plenty of water and recrystallised from dilute acetic acid when it came out as brick-red fine needles melting with decomposition at 246–47° (Biggs and Pope¹, 237° decomp.). It was readily soluble in sodium hydroxide exhibiting a bright green fluorescence much stronger than that exhibited by the tetrabromo derivative. Yield, almost quantitative. (Found: Br, 36.5; C₁₆H₁₀O₅Br₂ requires Br, 36.2%).

Tetraiodo-resorcinol-succinein.—

Resorcinol-succinein (0.5 g.) was dissolved in sodium hydroxide solution (2%; 15 c.c.) and treated with a solution of iodine (2.5 g.) in aqueous potassium iodide (4.5 g. in 10 c.c. of water). The solution assumed a bright red colour and lost all its original fluorescence. Excess of iodine in the solution was then destroyed by passing sulphur dioxide through it with cooling. The solution was poured into a slight excess of ice-cold dilute hydrochloric acid. The bright red precipitate was filtered, washed with water and ground up with dilute hydrochloric acid in a mortar. It was filtered and washed repeatedly with water. The product was a deep red micro-crystalline powder decomposing above 300°. It was readily soluble in

sodium hydroxide with no fluorescence. Yield, about 90%. (Found: I, 64.1; $C_{16}H_8O_5I_4$ requires I, 64.5%).

Mercuration of Resorcinol-succinein.—

Resorcinol-succinein (0.5 g.; 1 mol.) was dissolved in freshly prepared anhydrous methyl alcohol (20 c.c.) and treated with a solution of mercuric acetate (2.5 g.; about 4.5 mol.) in the same solvent (10 c.c.) containing a few drops of glacial acetic acid. Immediately, a bright red crystalline precipitate began to separate out even at the laboratory temperature. It was boiled under reflux for about 6 hours to complete the reaction and left overnight for complete precipitation. The precipitate was filtered, washed with plenty of anhydrous methyl alcohol containing glacial acetic acid to remove mercuric acetate completely. The product was finally purified by grinding with anhydrous methyl alcohol-glacial acetic acid mixture in a mortar. It was filtered and washed with anhydrous methyl alcohol. It was a deep red micro-crystalline powder decomposing above 300°. It was easily soluble in sodium hydroxide forming an orange red solution with a deep green fluorescence in dilute solutions. Yield: 2.0 g. Found: Hg, 60.7; $C_{24}H_{20}O_{13}Hg_4$ requires Hg, 60.9%).

Component (B): 2:4:2':4'-Tetrahydroxy-dibenzoylthane (II).—

The orange yellow residue insoluble in 5% hydrochloric acid was boiled several times with 5% hydrochloric acid to remove traces of resorcinol-succinein and then purified by crystallisation from a large quantity of alcohol. It came out as pale yellow rhombohedral prisms melting at 310–12° and gave an intense red colour with alcoholic ferric chloride; yield, 0.2 g. (Found: C, 63.4; H, 4.8; $C_{18}H_{14}O_6$ requires C, 63.6; H, 4.6%). When dissolved in concentrated sulphuric acid, it yielded a pale yellow solution which showed a pale green fluorescence in daylight. An alcoholic solution of the substance exhibited a weak green fluorescence which increased on the addition of dilute alkali. It was soluble in sodium hydroxide and ammonia in the cold and in warm sodium carbonate and bicarbonate solutions exhibiting a feeble green fluorescence.

Methyl ether of the diketone.—The diketone (1.0 g.) was dissolved in dry acetone (50 c.c.) and boiled under reflux with dimethyl sulphate (4 c.c.) and anhydrous potassium carbonate (25 g.) for about 15 hours. The solvent was then distilled off and the residue treated with water. The separated methyl ether was crystallised from acetone when it was obtained as colourless stout rectangular plates melting at 148–50°. (Found: C, 67.1; H, 6.3 OCH_3 , 34.8; $C_{20}H_{22}O_6$ requires C, 67.0; H, 6.1 and OCH_3 , 34.6%). It

was unaffected by treatment with cold alcoholic potash and hence was not an ester.

Oxime of the methyl ether.—This was prepared as usual using hydroxylamine hydrochloride and sodium acetate in aqueous alcoholic solution. The product was crystallised from a large quantity of alcohol when it came out as clusters of colourless rhombohedral prisms melting at 218–20°. (Found: C, 62.1; H, 5.8; $C_{20}H_{24}O_6N_2$ requires C, 61.9; H, 6.2%).

Ethyl ether of the diketone (II).—The diketone (1.0 g.) was ethylated using diethyl sulphate. The ethyl ether crystallised from acetone as colourless stout prisms melting at 159–60°. (Found: C, 69.6; H, 7.0; $C_{24}H_{30}O_6$ requires C, 69.6 and H, 7.2%). It was insoluble in dilute sodium hydroxide solution.

Acetate of the diketone (II).—The diketone was acetylated by boiling with acetic anhydride and a few drops of pyridine for about 15 minutes. The acetate crystallised from acetone as colourless short rectangular prisms and rods melting at 140–41°. (Found: C, 61.0; H, 4.8; $C_{24}H_{22}O_{10}$ requires C, 61.3 and H, 4.7%). It was insoluble in cold dilute alkali.

The Phenylhydrazone of (II) was prepared by boiling a mixture of the diketone (0.5 g.), phenylhydrazine hydrochloride (1.0 g.) and sodium acetate (2 g.) in dilute alcohol. The hydrazone was crystallised from dilute alcohol when it appeared as pale red rectangular plates melting with decomposition at 208°. (Found: C, 69.4; H, 5.0; $C_{28}H_{26}O_6N_4$ requires C, 69.7; H, 5.4%).

The 2:4-dinitrophenylhydrazone of (II) was obtained by using dinitrophenylhydrazine hydrochloride. When crystallised from alcohol it appeared as aggregates of reddish tiny prisms melting at 185–87°. (Found: C, 51.0; H, 3.5; $C_{28}H_{22}O_{12}N_8$ requires C, 50.8; H, 3.3%).

Orcinol-succinein.—

Succinic acid (5.0 g.) and anhydrous orcinol (10.0 g.) were intimately mixed and heated at 170° for $\frac{1}{2}$ hour and freshly fused zinc chloride (0.5 g.) then added with stirring. The reaction mixture was heated for another 3 hours, the temperature being maintained between 170–80°. After cooling it was treated with sodium hydroxide (100 c.c.; 2%) and filtered. The solution was acidified with ice-cold dilute hydrochloric acid avoiding excess. The precipitated fluorescein was filtered off and recrystallised from 5% hydrochloric acid when it came out as glistening dark crimson rectangular plates melting with decomposition at 259–60°. Yield, 6.8 g. (Found: C, 58.6; H, 6.4; loss on drying in vacuo at 150–60° for 4 hours 14.4; $C_{19}H_{16}O_5, 3H_2O$ requires C, 59.0; H, 6.0 and loss on drying 14.8%). It was easily soluble

in acetone and ethyl acetate, sparingly soluble in alcohol and insoluble in petroleum ether. In alkaline solution, it formed a deep red solution with a bright green fluorescence resembling that of resorcinol-phthalein. With alcoholic ferric chloride, it gave a dark brown colour. No by-product was obtained.

Tetrabromo-orcinol-succinein.—

Orcinol-succinein (0.5 g.) was dissolved in glacial acetic acid and brominated as in the previous case with excess of bromine in the same solvent. The tetrabromo-derivative was crystallised from glacial acetic acid when it came out in the form of deep red prisms and decomposed above 300°. Yield 1.0 g. (Found: Br, 50.8; $C_{18}H_{12}O_5Br_4$ requires Br, 51.0%). It was sparingly soluble in glacial acetic acid and other common organic solvents and readily soluble in alkaline solutions with a weak green fluorescence.

Mercuration of orcinol-succinein.—

Orcinol-succinein was mercurated using mercuric acetate as described under resorcinol-succinein. It was obtained as a deep red microscopic crystalline powder decomposing above 300°. [Found: Hg, 59.4; $C_{18}H_{12}O_5$ ($Hg.O.CO.CH_3$)₄ requires Hg, 59.6%].

Condensation of maleic anhydride and resorcinol: Isolation of resorcinol malein (V) and 2:4:2':4'-tetrahydroxy-dibenzoyl-ethylene (IV):—

Maleic anhydride (50 g.) and resorcinol (100 g.) were heated together at 150° for 2 hours. The reaction product was cooled and treated with water (300 c.c.) and stirred when a pale orange yellow precipitate (A) separated out from the dark red solution. It was filtered and washed with a small quantity of water. On concentrating the filtrate (B) and allowing it to stand, the malein (V) separated out as a crystalline solid melting at 250°. It crystallised from water as orange yellow rectangular prisms and rods melting at 268–70°. Yield. 4 g. (Found: C, 63.7; H, 4.3; loss on drying at 120° for 3 hours 5.8%; $C_{16}H_{10}O_5, H_2O$ requires C, 64.0; H, 4.0 and loss on drying 6.0%). It dissolved in dilute alkali giving a bright green fluorescence. In alcoholic solution it gave a green fluorescence and this was found even in sulphuric acid solution.

The residue (A) mentioned above gave only a feeble green fluorescence in alkaline solutions. It was sparingly soluble in hot water. The purification was effected by dissolving it in acetone and adding petroleum ether to the solution when a small quantity of a coloured impurity separated out, leaving the solution clear and colourless. The clear supernatant liquid was carefully decanted and the solution concentrated when it gave a pale yellow

crystalline product. Final purification was effected by crystallisation from aqueous acetone when the diketone (IV) came out as deep yellow rhombohedral prisms melting at 254–56° with decomposition. Yield, 75 g. (Found: C, 64.2; H, 4.2; $C_{16}H_{12}O_6$ requires C, 64.0 and H, 4.0%). It was soluble in sodium hydroxide forming a yellow solution with a very weak green fluorescence and gave a strong intense red colour with alcoholic ferric chloride. In concentrated sulphuric acid, it dissolved to give a pale yellow solution with a green fluorescence.

Methyl ether of (IV).—

The above diketone was boiled with dimethyl sulphate and anhydrous potassium carbonate in acetone solution for 20 hours. The product crystallised from alcohol as colourless rectangular plates melting at 139–41.° (Found: C, 67.2; H, 5.9; OCH_3 , 35.0; $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.6; and OCH_3 , 34.8%).

Phenylhydrazone of (IV).—

This was prepared as usual using phenylhydrazine hydrochloride. The hydrazone crystallised from alcohol as bright red long rectangular plates melting at 159–60°. (Found: C, 70.2; H, 5.2; $C_{28}H_{24}O_4N_4$ requires C, 70.0 and H, 5.0%).

Dinitrophenylhydrazone of (IV).—

This was prepared as usual using 2:4-dinitrophenylhydrazine hydrochloride. The hydrazone crystallised from alcohol as bright red stout rhombohedral prisms melting at 200–202°. (Found: C, 51.1; H, 3.3; $C_{28}H_{20}O_{12}N_8$ requires C, 50.9; H, 3.0%).

Acetate of (IV).—

The diketone (1.0 g.) was gently boiled with acetic anhydride (4 c.c.) and freshly fused and powdered sodium acetate (1.0 g.) for 4 hours. After cooling it was poured into water. The product was crystallised first from acetone and finally from alcohol when it came out as colourless rectangular plates melting at 198–200°. (Found: C, 61.3; H, 4.4; $C_{24}H_{20}O_{10}$ requires C, 61.5; H, 4.3%).

Tetrabromo-resorcinol-malein. —

The bromination was effected as before using excess of bromine in glacial acetic acid and resorcinol malein in the same solvent. It crystallised from glacial acetic acid as reddish brown rectangular prisms and rods decomposing above 300°. (Found: Br, 53.2; $C_{16}H_8O_5Br_4$ requires Br, 53.5%). It did not exhibit any fluorescence in alkaline solution.

Tetraiodo-resorcinol-malein.—

The iodination of resorcinol-malein was effected as described under resorcinol-succinein. The product was purified by grinding up with dilute hydrochloric acid, filtering and washing with water until it was free from acid. It was a deep reddish brown micro-crystalline powder decomposing at above 300°. (Found: I, 64·5; $C_{16}H_8O_5I_4$ requires I, 64·5%). It readily dissolved in dilute sodium hydroxide solution and emitted no fluorescence.

Mercuration of resorcinol-malein (V).—

This was effected as described under the mercuration of resorcinol succinein (I). The product was purified by grinding up with anhydrous methyl alcohol-glacial acetic acid mixture in a mortar. It was filtered and washed with anhydrous methyl alcohol. It was a deep red micro-crystalline powder decomposing above 300°. (Found: Hg, 61·0; $C_{24}H_{18}O_{13}Hg_4$ requires Hg, 61·0%). It was easily soluble in sodium hydroxide forming an orange red solution with a deep green fluorescence.

Condensation of succinic acid or anhydride with phenol: 4:4'-dihydroxy-dibenzoyl-ethane (VI).—

Succinic acid or anhydride (8 g.), phenol (20 g.) and freshly fused and powdered zinc chloride (2·0 g.) were intimately mixed and heated for 4 hours at 120°. The excess of phenol was then steam distilled. After cooling, the small amount of resin that separated out was removed and as no other solid product separated out, the solution was ether extracted. On concentration of the ether solution, the diketone was obtained as a colourless crystalline solid. It was recrystallised from ether when it appeared as colourless stout rhombohedral prisms melting at 190–92°; yield, 0·5 g. (Found: C, 71·0; H, 5·3; $C_{16}H_{14}O_4$ requires C, 71·1 and H, 5·2%). It dissolved easily in aqueous alkali forming a colourless solution and did not give any colour with alcoholic ferric chloride. With sulphuric acid it formed a pale orange red solution.

Condensation of maleic anhydride with phenol: 4:4'-dihydroxy-dibenzoyl-ethylene (VII).—

Maleic anhydride (7·0 g.), phenol (20·0 g.) and freshly fused and powdered zinc chloride (2·0 g.) were intimately mixed and heated for 4 hours at 120°. After cooling, it was poured into water (250 c.c.) and the excess of phenol steam distilled. A brown viscous liquid separated out which solidified on keeping for 24 hours. It was filtered and crystallised from 10% aqueous alcohol or a large quantity of water when it came out in the form of colourless rectangular plates melting with decomposition at 300°. (Found:

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C, 71.7; H, 4.9; $C_{16}H_{12}O_4$ requires C, 71.6 and H, 4.5%). It was highly soluble in acetone and alcohol. The product easily dissolved in sodium hydroxide without any colour and did not give any colour with alcoholic ferric chloride. Yield, 4.5 g.

The same product was also obtained by using maleic acid itself instead of its anhydride, its mixture with phenol was first heated for $\frac{1}{2}$ hour before adding zinc chloride. The presence of the condensing agent was essential in both cases.

4:4'-Dimethoxy-dibenzoyl-ethylene.—

The above diketone was methylated using dimethyl sulphate and anhydrous potassium carbonate in acetone solution by boiling for a period of 12 hours. It was crystallised from alcohol when it came out as colourless rectangular plates and prisms melting at 109–10°. (Found: C, 72.7; H, 5.7; $C_{18}H_{16}O_4$ requires C, 73.0 and H, 5.4%). It was insoluble in sodium hydroxide solution.

SUMMARY

Resorcinol condenses with succinic anhydride forming resorcinol-succinein as the main product and tetrahydroxy-dibenzoyl-ethane as a very minor by-product. Orcinol also gives a good yield of orcinol-succinein. These could be used conveniently for the preparation of halogen and mercury substituted derivatives. Resorcinol gives only a poor yield of the malein, the major condensation product with maleic anhydride being the diketone, tetrahydroxy-dibenzoyl-ethylene. Phenol does not give any isolable quantity of succinein or malein and only the corresponding diketones could be isolated by condensation with succinic anhydride and maleic anhydride. A number of derivatives of the diketones are described.

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