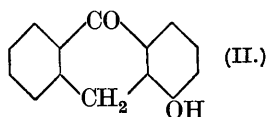
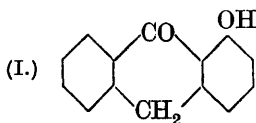


### XLIV.—Reduction Products of the Hydroxyanthraquinones. Part XI.

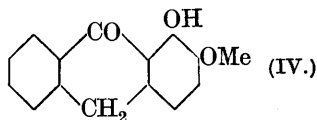
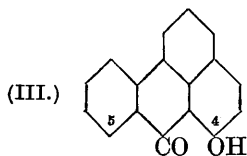
By EDWIN JOHN CROSS and ARTHUR GEORGE PERKIN.

WHEN unsymmetrical hydroxyanthraquinones are reduced, in general only one of the two theoretically possible hydroxyanthranols is produced; *e.g.*, 1-hydroxyanthraquinone yields 1-hydroxyanthranol (or anthrone) (I), there being no evidence of the simultaneous formation of the 4-hydroxy-compound (II).



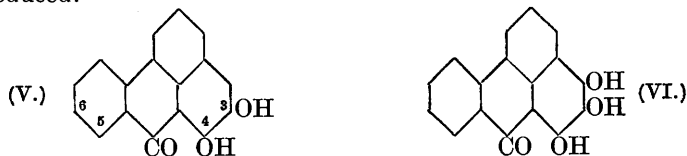
The anthrone formula, which is applicable to 1-hydroxyanthranol (Meyer and Sander, *Annalen*, 1920, **420**, 113) and possibly to other 1-hydroxyanthranols, is adopted in all cases throughout this paper for the sake of simplicity.

Although hitherto it has not been possible to speculate with any certainty as to the influence of the hydroxyl group or groups of hydroxyanthraquinones in definite positions on the production therefrom of this or that isomeric hydroxyanthranol, a determination of the exact structure of the latter has added considerably to our knowledge in this respect. For this purpose the conversion of hydroxyanthranol into hydroxybenzanthrone has been mainly studied, and the presence or absence of the  $\alpha$ -hydroxyl group in the latter ascertained by the employment of methyl iodide and alkali. Thus, when the hydroxybenzanthrone (III) derived from (I) is so treated, methylation does not occur, giving evidence that the former is, without doubt, the 4- or 5-hydroxy-compound (III), and the latter the 1-hydroxy-compound (Perkin and Spencer, *J.*, 1922, **121**, 474).



Although alizarin had hitherto been known to give but one anthranol (3 : 4-dihydroxyanthranol), Miller and Perkin (*J.*, 1925, **127**, 2684), employing stannous chloride and hydrochloric acid,

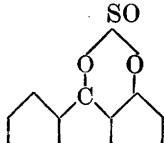
obtained from alizarin 2-methyl ether a mixture of 4-hydroxy-3-methoxy- and 1-hydroxy-2-methoxy-anthranol (IV). The constitution of the latter became evident from the fact that, by treatment with glycerol and sulphuric acid, *isobenzalazarin* (3:4- or 5:6-dihydroxybenzanthrone) (V) is obtained, a compound from which, by the reagents stated, only a monomethyl ether can be produced.



Adopting the same methods, it has been shown by Cross and Perkin (J., 1927, 1297) that the anthranols derived from anthrapurpurin, flavopurpurin, and anthragallol are respectively the 3:4:6-, 1:2:6-, and 1:2:3-trihydroxy-compounds, the last yielding 2:3:4-trihydroxybenzanthrone (VI).

The  $\alpha$ -hydroxyl group in hydroxybenzanthrones is not only resistant to methylation but is much less readily acetylated than the  $\alpha$ -hydroxyl of hydroxyanthraquinones: for instance, a fully acetylated derivative can be prepared from (V) only with difficulty, and from (VI), as yet, only a diacetyl compound has been obtained. Evidently, therefore, the chelate ring in  $\alpha$ -hydroxybenzanthrones possesses a much firmer character than that which is present in  $\alpha$ -hydroxyanthraquinones.

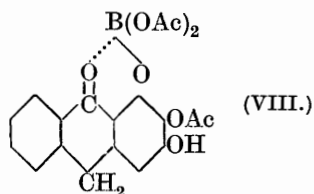
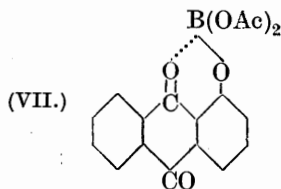
Green (J., 1927, 2341) suggests the employment of thionyl chloride as a reagent for the determination of the structure of hydroxyanthranols, in that ortho- and peri-hydroxyls when present in a phenol yield thionyl derivatives, whereas such compounds are not given by meta- and para-dihydric phenols (J., 1924, 125, 1450; 1926, 1428, 2198; 1927, 500, 554). In order to illustrate the utility of this method, he examined only three anthranols, *viz.*, 1-hydroxyanthranol (I), 4-chloro-1-hydroxyanthranol, and anthragallolanthranol. Of these, the first two only yielded thionyl compounds,

evidently of the type , whereas the last did not so

react. From this scanty evidence, and notwithstanding the proof given by Cross and Perkin (*loc. cit.*) to the contrary, this author concludes that anthragallolanthranol is not the 1:2:3-trihydroxyanthranol (1:2:3:9-tetrahydroxyanthracene) but the 2:3:4-

trihydroxyanthranol (1 : 2 : 3 : 10-tetrahydroxyanthracene). It appears at first sight somewhat strange that 1-hydroxyanthranol, which in reality is 1-hydroxyanthrone (Meyer and Sander, *loc. cit.*), reacts with thionyl chloride in the manner indicated, unless in these circumstances tautomerisation of the anthrone to the anthranol is presumed to occur.

It has been shown by Dimroth and Faust (*Ber.*, 1921, 54, 3020) that when  $\alpha$ -hydroxyanthraquinones are treated with boroacetic anhydride, boric esters are produced. 1-Hydroxyanthraquinone thus yields 1-hydroxyanthraquinone boroacetate (VII), and diboroacetates are given by 1 : 4- and 1 : 5-dihydroxyanthraquinones.



The compounds are decomposed by water, giving  $\alpha$ -hydroxyanthraquinone and boric and acetic acids. The application of this method to  $\alpha$ -hydroxyanthranols (anthrones) was tested first with 1-hydroxy-2-methoxyanthrone: a boroacetate, however, could not be prepared, for, although with the boiling reagent chemical alteration evidently occurred, in the cold a product of an indefinite character resulted. Anthragallolanthranol at first gave substances of an indefinite character, and it was only by the employment of special conditions that success was attained. Though different preparations of the orange crystalline product varied somewhat in composition, there could be no doubt that they essentially consisted of a *boroacetic ester* of 1 : 3-dihydroxy-2-acetoxyanthranol (VIII), and this result further confirms the statement of Cross and Perkin (*loc. cit.*) that the anthranol prepared by the reduction of anthragallol itself is the 1 : 2 : 3-trihydroxy-compound (IX).

The fact that, with stannous chloride and hydrochloric acid, 2-ethylcarbonatoalizarin gives 1-hydroxy-2-ethylcarbonatoanthranol, apparently as sole product (Perkin and Story, J., 1929, 1405), suggested as desirable a study of the influence, if any, of the acyloxy-group in acyloxyanthraquinones on the orientation of the hydroxy- or acyloxy-groups in the anthranols derived therefrom by reduction. The method here adopted, which consists in adding stannous chloride-hydrochloric acid to a hot solution of the acyl compound in acetic acid, has given results of interest. From triacetylanthragallol, thus treated, two anthranols are obtained: (a) the 1 : 2 : 3-trihydroxy-compound (IX), present in but small amount, and (b)

the main product, which consists, as shown below, of the hitherto unknown 2 : 3 : 4-trihydroxy-9-anthranol (X).



As the acetoxy-group is so readily hydrolysed in the circumstances, it is remarkable that such a process can be applied to acetyl compounds. That the elimination of the acetyl group here only occurs when reduction is complete and not, at least to any extent, prior to this process in most instances, is due to the extreme rapidity of the latter reaction, for this in general occupies but a few seconds, though in practice a somewhat longer digestion has usually been employed. If stannous chloride-hydrochloric acid is added to a warm solution of the acetoxyanthraquinone in acetic acid and the mixture is kept without further heating, complete reduction usually occurs over-night.

In order to ascertain the constitution of (X), it was heated with glycerol and sulphuric acid, and there was thus obtained, with considerable difficulty and in small amount, a trihydroxybenzanthrone, here termed *benzanthragallol*. This compound, which differs considerably in properties from the *isobenzanthragallol* (VI) derived from 1 : 2 : 3-trihydroxy-9-anthranol, readily gives a *trimethyl* ether when treated with methyl iodide and alkali, whereas the isomeride does not. Benzanthragallol, therefore, has the constitution (XI), and can thus have only originated from the 2 : 3 : 4-trihydroxy-9-anthranol (X).



A complete proof is thus afforded that, on reduction, anthragallol itself gives 1 : 2 : 3-trihydroxy-9-anthranol, and not, as suggested by Green, the 2 : 3 : 4-trihydroxy-9- (or 1 : 2 : 3-trihydroxy-10-) anthranol. It is moreover evident that thionyl chloride is hardly a trustworthy reagent for the detection of the 1-hydroxyl group in hydroxyanthranols.

The reduction of 2 : 3-diacetylanthragallol in a similar manner was now studied, the result being the production of 1 : 2 : 3-trihydroxy-9-anthranol (IX) identical with that given by anthragallol itself.

In order to illustrate more clearly the effect of the acetyl and other groups in this connexion, the results of this section of the investigation are embodied in the following table, and here, for purposes of comparison, the reduction products given by the free hydroxyanthraquinones are also included.

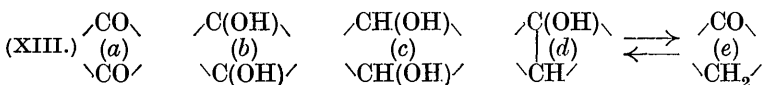
Anthraquinones.	Anthranols obtained by reduction.	
Anthragallol	1 : 2 : 3-Trihydroxy-9-anthranol	
Triacetylanthragallol	" "	2 : 3 : 4-Trihydroxy-9-anthranol
Diacetylanthragallol	" "	
Tribenzoylanthragallol		Dibenzoyl-2 : 3 : 4-tri-hydroxy-9-anthranol
Dibenzoylanthragallol	Dibenzoyl-1 : 2 : 3-tri-hydroxy-9-anthranol Monobenzoyl-1 : 2 : 3-tri-hydroxy-9-anthranol	
Triethylcarbonato-anthragallol	2 : 3-Diethylcarbonato-1-hydroxy-9-anthranol	Dicarbethoxy-2 : 3 : 4-tri-hydroxy-9-anthranol
Diethylcarbonato-anthragallol	" "	
	2-Ethylcarbonato-1 : 3-dihydroxy-9-anthranol	
Alizarin : (acid solution)	1 : 2-Dihydroxy-9-anthranol	3 : 4-Dihydroxy-9-anthranol
(alkaline solution)		" "
2-Acetylalizarin	" "	" "
Diacetylalizarin	" " (trace)	" "
Alizarin 2-methyl ether	1-Hydroxy-2-methoxy-9-anthranol	4-Hydroxy-3-methoxy-9-anthranol
Acetylalizarin 2-methyl ether		" "
1-Acetoxyanthraquinone		4-Hydroxy-9-anthranol
1 : 8-Dihydroxy-anthraquinone	1 : 8-Dihydroxy-9-anthranol	
1 : 8-Diacetoxy-anthraquinone		4 : 5-Dihydroxy-9-anthranol (XII)
1 : 2 : 6-Trihydroxy-anthraquinone	1 : 2 : 6-Trihydroxy-9-anthranol	

Although acetoxyanthraquinones are reduced very rapidly (*loc. cit.*) by the method here employed, the reduction of ethylcarbonatoanthraquinones (or at least of triethylcarbonatoanthragallol) occurs more slowly, because, though, in the circumstances employed, the carbethoxy-group is less readily eliminated than the acetyl group, it is apparent that, in the instance above cited, some hydrolysis with removal of the ethylcarbonato-group has taken place, both before and after the reduction. Thus, under the conditions employed (see above), triethylcarbonatoanthragallol (A) yields in part diethylcarbonatoanthragallol (B). (A) on reduction

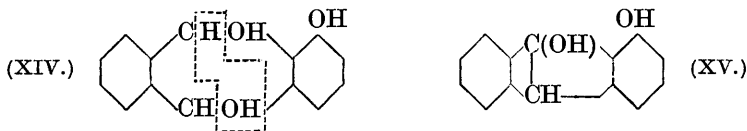
gives 2:3:4-triethylcarbonatoanthrone, passing by subsequent hydrolysis to the diethyl compound, whereas from (B) 1-hydroxy-2:3-diethylcarbonatoanthrone is obtained.

Among the points of interest indicated above are the preparation, not only of the two new hydroxyanthranols (II) and (X), but of 4-hydroxy-3-methoxy- and 1:2-dihydroxy-9-anthranols, compounds hitherto not readily obtained, in almost quantitative yield. That 1:2-dihydroxy-9-anthranol can also be prepared in this way directly from alizarin—though in conjunction with the 3:4-dihydroxy-compound—has also been ascertained for the first time, and this affords evidence that reduction of an  $\alpha$ -hydroxyanthraquinone in acid solution and in an alkaline medium does not of necessity proceed in an identical manner in both cases.

The results of this investigation indicate that when hydroxyanthraquinones containing an  $\alpha$ -hydroxy-group are reduced in an acid solution in the manner indicated, the  $\alpha$ -hydroxy-group as a rule is found to be in the 1-position adjacent to the carbonyl group, or to the hydroxyl in the 9-position of the resulting hydroxyanthrone or hydroxyanthranol. If, on the other hand, the  $\alpha$ -hydroxyl of the hydroxyanthraquinone is acylated before reduction, the reverse is the case, this hydroxyl then occupying the 4-position in the product. In other words, the carbonyl adjacent to the acyloxy-group in  $\alpha$ -acyloxyanthraquinones is preferably reduced: this is clearly shown by (I) and (II), which represent respectively the reduction products of 1-hydroxy- and 1-acetoxy-anthraquinone. If in these cases the reaction proceeds according to the usually accepted scheme (XIII), an explanation of the fact cited above, in the light of our present knowledge, is difficult, because it is in no way clear why, in the

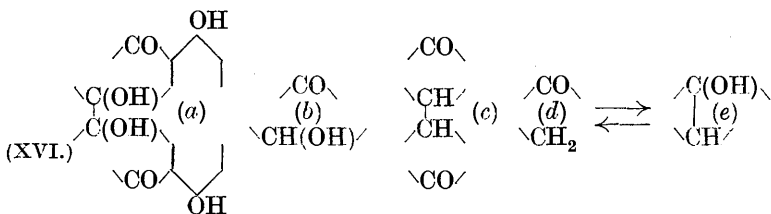


change of (XIV) into (XV) ( $c-d$ ) during the reduction of 1-hydroxyanthraquinone to 1-hydroxyanthrone (or anthranol), water should be split off only in the manner indicated, and not in both directions



with the simultaneous formation of 1- and 4-hydroxyanthranols. It seems reasonable to infer that the influence dominating the formation of 1-hydroxyanthranols from  $\alpha$ -hydroxyanthraquinones by acid reduction is the chelate linkage between the  $\alpha$ -hydroxyl and

the carbonyl group of the latter. This renders the latter immune from reduction, a fact which can also be expressed by saying that the chelate linkage remains intact in the series of changes involved. Such a suggestion can be indicated (XVI) by the stages (a) dihydroxypinacol, (b) hydroxyanthranol, (c) dianthrone, (d) anthrone, (e) anthranol. On the other hand, when the  $\alpha$ -hydroxy-group is



acylated the chelate linkage is destroyed, and the adjacent carbonyl group is no longer immune from reduction. Of interest in this respect is the statement of Meyer and Sander (*loc. cit.*) that 1-hydroxy-9-anthranol is produced when 1-hydroxyanthraquinone is reduced in acid solution, and that only by the use of alkaline media could the corresponding anthraquinol be obtained. If the scheme outlined above is to be considered, at least in the main, correct, proof of the formation of hydroxydianthrone (stage c) during the reduction process is necessary, and though there have been indications during more recent work, in special instances, of the presence of such compounds in the final products, further investigation is necessary to determine if their formation in this manner from  $\alpha$ -hydroxyanthraquinones is of general occurrence.

An exception to the rule that  $\alpha$ -hydroxyanthraquinones yield on reduction 1-hydroxyanthrones (or anthranols) is the 1:2:7-trihydroxy-compound (anthrapurpurin) (*loc. cit.*), which gives both with stannous chloride-hydrochloric acid and with aqueous ammonia and zinc dust, 3:4:6-trihydroxy-9-anthranol. In the case of anthrapurpurin, however, two factors can be considered to influence the reaction: (a) the 1-hydroxy-group and (b) the remote  $\beta$ -hydroxy-group in the 7-position. Whereas it is to be anticipated that the former (compare alizarin) will tend, though only in part (*loc. cit.*), to give an  $\alpha$ -hydroxyanthrone, the latter (compare 2-hydroxy- and 2-acetoxy-anthraquinone, which, as experiment has shown, both yield 3-hydroxyanthranol as sole product) will desire to take up the 6-position in the resulting hydroxyanthranol. The latter influence evidently predominates in the present instance: this point will be further discussed in a subsequent communication.

In the German patent 187495 (Friedländer's "Fortschritte," IX,

816) two methods are given for the preparation of hydroxybenzanthrones : (a) the action of glycerol and sulphuric acid on hydroxyanthranols and (b) the similar treatment of hydroxyanthraquinones in the presence of reducing agents. That in these circumstances the product of the reduction, according to the patent, of a hydroxyanthraquinone and the anthranol derived therefrom by alkaline reduction, do not necessarily give the same hydroxybenzanthrone is obvious from the results of the present investigation, and indeed the properties given in the patent of the hydroxybenzanthrone derived from alizarin differ markedly from those of the 7 : 8-dihydroxy-compound (Perkin, J., 1920, 117, 702) which is obtained in a similar manner from 3 : 4-dihydroxyanthranol (deoxyalizarin). Evidently, therefore, the former product is either 3 : 4- or 5 : 6-dihydroxybenzanthrone. Turski and Grynwasser (*Rocz. Chem.*, 1929, 9, 78) purport to have decided this point by synthetical methods and describe these compounds as melting at 285° and 185° respectively. Their paper \* is remarkable in that it consists merely of a series of statements. It contains no account of the properties or the melting points of the new compounds which were prepared for the purpose of these syntheses, and but one analysis seems to have been performed, the figures of which are not stated. The results of these authors, at least in regard to one or other of the dihydroxybenzanthrones they describe, are not in harmony with those of Miller and Perkin (*loc. cit.*), who obtained *isobenzalizarin* (V) from 1-hydroxy-2-methoxyanthranol; for this, which melts at 265°, is either the 3 : 4- or the 5 : 6-dihydroxy-compound. A reinvestigation has confirmed the correctness of the melting points previously given both for this compound and for its acetyl derivative (243—245°). The action of glycerol and sulphuric acid on alizarin in the presence of aniline sulphate was now studied, with the result that the crude product obtained resembled that described in the patent, more especially in regard to its giving strongly fluorescent solutions both in sulphuric acid and in dilute alkali. This substance is, however, a mixture, for on treatment by the method described below, a more sparingly soluble fraction can be isolated in small amount, which is devoid of fluorescent property. This yielded an acetyl compound melting at 243—245°, and without doubt consisted of *isobenzalizarin*. There is no reason why alizarin, in the circumstances, should not yield isomeric hydroxybenzanthrones, and if this is so, it is possible that the compound, m. p. 185°, described by Turski and Grynwasser as 5 : 6-dihydroxybenzanthrone, which gives fluorescent solutions in the manner indicated, is present in

\* For a translation of this paper, which is written in Polish, we are indebted to the kindness of Mrs. J. W. McLeod of Leeds.



the more soluble fraction of the reaction product. Should such be the case, then *isobenzalizarin* is 3 : 4-dihydroxybenzanthrone, and the nature of the compound they describe as melting at 285°, and to which they ascribe the same constitution, is not clear.

#### EXPERIMENTAL.

*Reduction of Triacetylanthragallol.*—To a boiling solution of triacetylanthragallol (10 g.) in acetic acid (100 c.c.), stannous chloride (40 g.) dissolved in warm hydrochloric acid (100 c.c.)\* was added. The pale yellow liquid darkened, became lighter when boiled for a short time, and deposited crystalline 2 : 3 : 4-trihydroxy-9-anthranol (X). After cooling, this was collected, washed with a mixture of acetic and hydrochloric acids and with water, and dried (yield, 4.3 g.). Addition of water to the filtrate gave a precipitate (1.5 g.) of which the colour reactions and the m. p. of the monoacetyl derivative, m. p. 239—240° (decomp.) (Breare and Perkin, J., 1923, 123, 2607), showed that it was 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol). The total yield of anthranols (5.8 g.) represents 91.6% of the theoretical amount.

2 : 3 : 4-Triacetoxy-9-anthranyl acetate was readily obtained by digesting the 2 : 3 : 4-trihydroxy-compound with boiling acetic anhydride and pyridine for a short time and adding alcohol to the product after cooling. The crystals obtained formed colourless prisms, m. p. 199—201°, after recrystallisation from alcohol-acetic acid (Found : C, 64.2; H, 4.45;  $C_2H_4O_2$ , 58.3.  $C_{22}H_{18}O_8$  requires C, 64.4; H, 4.4;  $C_2H_4O_2$ , 58.5%).

2 : 3 : 4-Trihydroxy-9-anthranol can be obtained only in a crude condition and of a deep green colour when the acetyl compound is hydrolysed with hydrochloric acid in the usual manner. If, however, a solution of the acetyl compound in boiling acetic acid is digested with half its volume of stannous chloride-hydrochloric acid until crystals commence to separate, the anthranol is obtained in needles which have, at most, a pale greenish tint. When heated, it gradually darkens, does not melt below 300°, and at this temperature is greenish-black (Found : C, 69.4; H, 4.2.  $C_{14}H_{10}O_4$  requires C, 69.4; H, 4.1%). The possibility, suggested by its high melting point, that this compound might be a dianthrone rather than an anthrone (anthranol) was disproved by a molecular-weight determination of the tetra-acetyl compound by the cryoscopic method with naphthalene as solvent (Found : *M*, 400.  $C_{22}H_{18}O_8$  requires *M*, 410. As the colourless solution, which has a faint blue fluorescence, gradually darkens, the initial readings only are trustworthy).

\* This concentration of stannous chloride in hydrochloric acid was employed throughout the investigation.

2 : 3 : 4-Trihydroxy-9-anthranol gives in 10% aqueous sodium hydroxide an orange solution which becomes yellow and finally brown in air : in the same circumstances, 1 : 2 : 3-trihydroxy-9-anthranol gives an orange liquid which eventually develops a deep violet tint. Again, the latter in alcoholic solution gives with benzoquinone violet crystals of anthragallol dianthronequinone (Breare and Perkin, *loc. cit.*), but the 2 : 3 : 4-trihydroxy-compound is devoid of this characteristic. When oxidised with chromic acid in acetic acid solution, 2 : 3 : 4-triacetoxy-9-anthranyl acetate yielded orange crystals, m. p. 218—220°; these probably consisted of 2 : 3-diacetylanthragallol, as triacetylanthragallol was obtained from them by acetylation. Attempts to prepare a dianthrone from 2 : 3 : 4-trihydroxy-9-anthrone have been unsuccessful.

*Benzanthragallol*.—A mixture of 2 : 3 : 4-trihydroxy-9-anthranol (1 g.), sulphuric acid (8 c.c.), water (6 c.c.), and glycerol (2 g.) was heated with stirring to 120—125° during 20 minutes, and kept there for the same period. The product was poured into water, the washed precipitate dried and digested with alcohol, the concentrated solution poured into ether, and the ethereal solution well washed. Evaporation gave a brown residue, from which, by acetylation with acetic anhydride and pyridine, minute yellow crystals (0.05—0.07 g.) were obtained. These were again acetylated, crystallised from acetic acid, and, being still impure, hydrolysed with hydrochloric acid in the usual manner. The product was dissolved in alcohol, and boiling water added to the filtered solution, which caused the separation of small orange-yellow prisms. These gradually darkened above 200° and became black at about 290° without any sign of fusion (Found : C, 73.0; H, 3.8.  $C_{17}H_{10}O_4$  requires C, 73.4; H, 3.6%). This substance, *benzanthragallol*, dissolves in sulphuric acid with a crimson, and in 1% caustic soda solution with a violet colour which quickly fades to a yellow tint in air. With 10% caustic soda solution, a deep blue colour is obtained which becomes green and then yellow in air. Benzanthragallol dyes mordanted woollen cloth in shades distinct from those given by anthragallol and by *isobenzanthragallol*, although they approximate in depth to those given by the former colouring matter. Orange, orange-brown, red-brown, and dark brown shades are given by tin, aluminium, chromium, and iron mordants respectively.

*Triacetylbenzanthragallol*, prepared in the usual manner, gives a fluorescent solution in acetic acid and crystallises therefrom in pale yellow needles, m. p. 221—223° (Found : C, 68.3; H, 4.1;  $C_{17}H_{10}O_4$ , 68.5.  $C_{23}H_{16}O_7$  requires C, 68.3; H, 4.0;  $C_{17}H_{10}O_4$ , 68.8%).

*Methylation*. To a boiling mixture of triacetylbenzanthragallol

(0.5 g.) in methyl alcohol (7.5 c.c.) and methyl iodide (3 c.c.), caustic potash (0.5 g.) \* in methyl alcohol was added during 12 hours. The product was concentrated, poured into ether, insoluble resinous matter removed, and the ethereal solution washed with dilute alkali and evaporated. The residue, crystallised first from benzene and then from alcohol, yielded lemon-yellow, hair-like needles (0.07 g.), m. p. 143—144° (Found : C, 74.6; H, 5.1; CH<sub>3</sub>, 13.9. C<sub>20</sub>H<sub>16</sub>O<sub>4</sub> requires C, 75.0; H, 5.0; CH<sub>3</sub>, 14.1%). *Benzanthragallol trimethyl ether* can also be prepared by methylating benzanthragallol with methyl sulphate in the usual manner. Its yellow ethereal and alcoholic solutions have a green fluorescence.

*Reduction of 2 : 3-Diacetylanthragallol.*—On treatment of this compound with stannous chloride–hydrochloric acid by a similar method to that employed with triacetylanthragallol, only 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol) was produced.

*Tribenzoylanthragallol.*—Dibenzoylanthragallol (see below) (2 g.), dissolved in pyridine (6 c.c.), was treated with benzoyl chloride (1 c.c.); crystals (2.3 g.) separated, and after dilution with an equal volume of alcohol these were removed and recrystallised from benzene–alcohol, pale yellow prisms, m. p. 213—215°, being obtained (Found : C, 73.8; H, 3.35. C<sub>35</sub>H<sub>20</sub>O<sub>8</sub> requires C, 73.9; H, 3.5%).

*Reduction.* To *tribenzoylanthragallol* (1 g.) in boiling acetic acid (50 c.c.), a boiling solution of stannous chloride–hydrochloric acid (25 c.c.) was added; the green precipitate first formed became colourless and crystalline after a few minutes' boiling. When cool, the crystals (0.5 g.) were removed (filtrate A), washed with hydrochloric acid and water, and recrystallised from acetone, almost colourless prisms containing acetone of crystallisation being obtained. When freed from solvent of crystallisation, these melted at 212—214° (Found : C, 74.4; H, 4.1; C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 55.6. C<sub>28</sub>H<sub>18</sub>O<sub>6</sub> requires C, 74.7; H, 4.0; C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 54.2%). A further quantity of this substance was isolated from filtrate A by dilution with water; the precipitate was collected, washed with hydrochloric acid and water, dried, and dissolved in boiling alcohol, from which crystals (0.25 g.) separated on cooling.

In order to eliminate the benzoyl groups from this compound, *dibenzoyl-2 : 3 : 4-trihydroxy-9-anthrone* (or *anthranol*), it was suspended in methyl alcohol, caustic soda solution added in small amount, and the mixture boiled for a few seconds. Acidification now yielded a dark purple precipitate, which was extracted with sodium bicarbonate solution to remove benzoic acid, dried, and acetylated. The product, repeatedly crystallised from alcohol—

\* Commercial stick. Theory requires 0.415 g. KOH for hydrolysis of the acetoxy-groups and formation of the trimethyl ether.

acetic acid, was obtained as colourless prisms, identical (mixed melting point) with 2 : 3 : 4-triacetoxy-9-anthranyl acetate.

*Dibenzoylanthragallol*.—Benzoyl chloride (2.3 c.c.) was slowly added to anthragallol (2 g.) in pyridine (10 c.c.) and after a while the solution was diluted with alcohol (10 c.c.). Crystals (2.5 g.) separated, and on recrystallisation from benzene were obtained as yellow leaflets, m. p. 204—206°. As this melting point is very similar to that of tribenzoylanthragallol (m. p. 213—215°), a determination of the molecular weight was necessary (Found : C, 72.4; H, 3.6; *M*, 453.  $C_{28}H_{16}O_7$  requires C, 72.4; H, 3.45%; *M*, 464).

*Reduction*. To a boiling solution of *dibenzoylanthragallol* (1 g.) in acetic acid (60 c.c.), stannous chloride–hydrochloric acid (20 c.c.) was added slowly in order to avoid precipitation and the mixture was boiled for 5 minutes. On cooling, crystals (0.6 g.) were gradually deposited (filtrate A); these were washed with hydrochloric acid and then with water, and recrystallised from acetic acid, very pale yellow needles, m. p. 188—190°, being obtained (Found : C, 74.8; H, 4.0.  $C_{28}H_{18}O_8$  requires C, 74.7; H, 4.0%).

This substance, *dibenzoyl-1 : 2 : 3-trihydroxyanthrone* (or *anthranol*), suspended in boiling alcohol, was treated with a few drops of caustic soda solution (10%). The deep yellow liquid first formed quickly became brown and from this by acidification and dilution with water a dark violet precipitate separated. This was collected, extracted with sodium bicarbonate solution to remove benzoic acid, and acetylated with a mixture of equal parts of acetic anhydride and acetic acid. Crystals separated as the boiling proceeded, and these, which after recrystallisation from much acetic acid melted at 239—240° (decomp.), consisted without doubt (mixed melting point) of monoacetyl-1 : 2 : 3-trihydroxyanthrone (or anthranol).

From the filtrate (A), on dilution with water, a precipitate (0.2 g.) separated. This, repeatedly crystallised from alcohol–acetic acid, gave colourless plates, m. p. 213—216° (decomp.) (Found : C, 72.7; H, 4.2.  $C_{21}H_{14}O_5$  requires C, 72.8; H, 4.05%). As this compound on alkaline hydrolysis yielded an anthranol having the characteristic properties of the 1 : 2 : 3-trihydroxy-compound, it was evidently *monobenzoyl-1 : 2 : 3-trihydroxyanthrone* (or *anthranol*).

*Triethylcarbonatoanthragallol*.—Diethylcarbonatoanthragallol (Perkin and Storey, J., 1928, 242) (6 g.) was dissolved in a mixture of pyridine (3 c.c.) and benzene (60 c.c.) and, after partial cooling, ethyl chloroformate (12 c.c.) was added all at once to the stirred solution. Viscid matter was gradually deposited, and after addition of charcoal the mixture was boiled, and the liquid filtered and evaporated to dryness with stirring. The residue, after being

washed with alcohol, crystallised from alcohol-acetic acid in very pale yellow prisms (5.9 g.), m. p. 103—105° (Found : C, 58.4; H, 4.3.  $C_{23}H_{20}O_{11}$  requires C, 58.5; H, 4.2%).

If a suspension of *triethylcarbonatoanthragallol* in cold pyridine is kept over-night, it is converted without apparent solution into the diethylcarbonato-derivative. Tribenzoylanthragallol is, however, not thus affected. Diethylcarbonatoanthragallol is again produced when a cold acetic acid solution of the triethylcarbonato-compound is treated with stannous chloride-hydrochloric acid, and the mixture kept over-night. This accounts for the fact (see below) that, when triethylcarbonatoanthragallol is reduced in the manner indicated, the products are identical with those given by the diethylcarbonato-derivative.

*Reduction.* To a boiling solution of triethylcarbonatoanthragallol (4 g.) in acetic acid (40 c.c.), a boiling solution of stannous chloride-hydrochloric acid (40 c.c.) was added. The precipitate first formed rapidly redissolved and the deep orange solution gradually became pale yellow. After 2 days, the crystals (0.9 g.) (filtrate A) were removed and recrystallised from alcohol-acetic acid, pale yellow prisms, m. p. 131—132°, being obtained (Found : C, 62.4; H, 4.9.  $C_{20}H_{18}O_8$  requires C, 62.2; H, 4.7%).

The removal of the carbethoxy-groups from this compound, which evidently consisted of *1-hydroxy-2:3-diethylcarbonato-9-anthranol*, and the acetylation of the product were carried out as with dibenzoyl-1:2:3-trihydroxyanthranol, monoacetyl-1:2:3-trihydroxy-9-anthranol being obtained.

Addition of water to filtrate (A), which had a strong odour of ethyl acetate, gave a resinous precipitate. This, after being washed, was dissolved in a little alcohol; the crystals (1 g.) obtained, on recrystallisation from alcohol, yielded colourless needles, m. p. 156—158° (Found : C, 62.1; H, 4.8.  $C_{20}H_{18}O_8$  requires C, 62.2; H, 4.7%). As this substance gave 2:3:4-triacetoxy-9-anthranol acetate by alkaline hydrolysis and subsequent acetylation, it consisted of *dicarbethoxy-2:3:4-trihydroxy-9-anthranol* (or *anthrone*).

*Diethylcarbonatoanthragallol.*—The method employed for the preparation of this compound differed somewhat from that given by Perkin and Storey (*loc. cit.*). To anthragallol (5 g.) in hot pyridine (20 c.c.), ethyl chloroformate (6.5 c.c.) was slowly added, followed, after cooling, by alcohol; the crystals obtained melted at 174—175° after recrystallisation from acetic acid.

*Reduction.* A boiling solution of stannous chloride-hydrochloric acid (120 c.c.) was added to diethylcarbonatoanthragallol (6 g.) in boiling acetic acid (120 c.c.). Next day, the crystals (2.4 g.) which had separated were collected (filtrate A) and repeatedly crystallised

from alcohol-acetic acid. The product was identical with the diethylcarbonato-1 : 2 : 3-trihydroxy-9-anthrone (mixed melting point) prepared in part (see above) by the reduction of triethylcarbonatoanthragallol.

From the filtrate (A) by addition of water a precipitate was obtained which, when digested with alcohol, yielded crystals (1 g.); these, recrystallised from acetic acid, gave almost colourless prisms, m. p. 218—219° (decomp.) (Found : C, 64·9; H, 4·7.  $C_{17}H_{14}O_6$  requires C, 65·0; H, 4·5%). Alkaline hydrolysis gave 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol)—evidence that the compound was its *monocarbethoxy*-derivative. From the alcoholic filtrate, only resinous matter could be isolated.

*Reduction of Monoacetylalizarin.*—To monoacetylalizarin (5 g.) in boiling acetic acid (50 c.c.), boiling stannous chloride-hydrochloric acid (50 c.c.) was added, and the digestion continued for a few minutes. The mixture slowly deposited pale orange plates of 1 : 2-dihydroxyanthrone (3 g.), which, after recrystallisation from alcohol, melted at 149—151° (Found : C, 74·7; H, 4·7. Calc. for  $C_{14}H_{10}O_3$  : C, 74·3; H, 4·4%). Acetylation in the usual manner gave 1 : 2-diacetoxy-9-anthranyl acetate, which crystallised from alcohol-acetic acid in colourless plates, m. p. 185—187° (Found : C, 68·1; H, 4·8.  $C_{20}H_{16}O_6$  requires C, 68·2; H, 4·5%).

The filtrate from the reduction mixture gave a further 0·4 g. of 1 : 2-dihydroxyanthrone on addition of water.

*Reduction of Diacetylalizarin.*—Stannous chloride-hydrochloric acid (50 c.c.) was added to diacetylalizarin (5 g.) in boiling acetic acid (50 c.c.), and the mixture boiled for a few minutes. The liquid, at first orange-red, soon became lighter in colour and, on keeping, deposited orange needles consisting apparently of the oxonium salt. These were removed (filtrate A) and decomposed by digestion with boiling water, yielding a pale yellow product (2·35 g.) which was shown to be deoxyalizarin by the melting point of its acetyl compound in admixture with acetyldeoxyalizarin.

The filtrate A, on dilution with water, gave a precipitate (0·35 g.) (filtrate B) of 1 : 2-dihydroxyanthrone, identified in the form of its acetyl derivative, m. p. 185—187°.

From the filtrate B, by saturation with sodium chloride, a further amount (0·65 g.) of deoxyalizarin was isolated.

*Reduction of Acetylalizarin 2-Methyl Ether.*—A solution of the ether (30 g.) in boiling acetic acid (300 c.c.) was slightly cooled, and stannous chloride-hydrochloric acid (120 c.c.) then added. An orange precipitate immediately separated which became crystalline and lighter in colour on keeping. After 60 hours, the crystals (22 g.) were collected : they consisted, without doubt, of 4-hydroxy-

3-methoxyanthranol (Miller and Perkin, *loc. cit.*). From the acid filtrate, a trifling amount of the same compound could be isolated.

*Reduction of Alizarin.*—To a boiling solution of alizarin (2 g.) in acetic acid (100 c.c.), hot stannous chloride–hydrochloric acid (100 c.c.) was added and the mixture was boiled for a few minutes and then diluted with an equal volume of boiling water. On cooling, crystals (0.8 g.) of 1:2-dihydroxyanthrone separated; after recrystallisation from alcohol, they melted at 149–151°. The filtrate was further diluted with water and saturated with sodium chloride, the precipitate collected and dissolved in a little alcohol, and the solution treated with boiling water. On cooling, crystals (0.5 g.) separated having all the properties of 3:4-dihydroxy-anthranol.

When alizarin is digested with stannous chloride–hydrochloric acid in the absence of acetic acid (compare Goodall and Perkin, J., 1924, **125**, 473), a viscid mass is obtained, reduction, at least in part, proceeding beyond the anthranol stage. From the product, which is readily soluble in alcohol, only 3:4-dihydroxy-9-anthranol in trifling amount has hitherto been isolated.

*Reduction of 1-Acetoxyanthraquinone.*—To 1-acetoxyanthraquinone (2 g.) in hot acetic acid (15 c.c.), stannous chloride–hydrochloric acid (12 c.c.) was added, causing a deposit to separate (stage A). This, on further heating, yielded an orange-brown liquid, which rapidly became pale yellow and then deposited crystals. These were collected after 12 hours and recrystallised, first from acetic acid containing stannous chloride–hydrochloric acid, and then from toluene. The almost colourless, flat needles of 4-hydroxy-9-anthranol obtained melted at 240–242°. If the mixture at stage A is kept in the cold for 2 days, complete conversion into the anthranol also occurs without further heating (Found : C, 79.7; H, 4.9.  $C_{14}H_{10}O_2$  requires C, 80.0; H, 4.8%). From the reduction mother-liquors, a trace of the same compound only could be isolated, and there was no evidence of the formation of the isomeric 1-hydroxy-9-anthrone. *Acetyl-4-hydroxy-9-anthranol*, prepared in the usual manner, forms colourless prisms, m. p. 173–175°. The alcoholic solution has a faint blue fluorescence (Found : C, 73.4; H, 4.7.  $C_{18}H_{14}O_4$  requires C, 73.5; H, 4.8%).

*Reduction of Diacetylchryszin.*—To diacetylchryszin (4.5 g.) in boiling acetic acid (150 c.c.), stannous chloride–hydrochloric acid (100 c.c.) was added. The crystals which separated on cooling were collected (yield, 3.5 g.) and crystallised from alcohol or nitrobenzene, from which solvents 4:5-dihydroxy-9-anthranol separated in almost colourless leaflets or prismatic needles respectively. These darkened

at 250° and melted at about 293—295° (Found : C, 74.0; H, 4.6.  $C_{14}H_{10}O_3$  requires C, 74.3; H, 4.4%).

*Acetyl-4:5-dihydroxy-9-anthranol* crystallises from acetic anhydride in needles, m. p. 220—222°, which gradually develop a brownish-black tint on exposure to sunlight (Found : C, 67.7; H, 4.5.  $C_{20}H_{16}O_6$  requires C, 68.2; H, 4.5%). Sulphuric acid dissolves it to form a brown liquid which slowly becomes green and finally orange.

*Reduction of 2-Acetoxyanthraquinone.*—To 2-acetoxyanthraquinone (2 g.) in acetic acid (15 c.c.), stannous chloride–hydrochloric acid (15 c.c.) was added, and the solution boiled for 5 minutes. The crystals which separated on cooling melted at 198—200° and evidently consisted of 3-hydroxy-9-anthranol, for on acetylation the acetyl compound, m. p. 155—157°, was produced. A further amount of the same substance was contained in the reduction mother-liquor, from which also the acetyl compound was prepared.

*Formation of isoBenzalizarin from Alizarin.*—A mixture of alizarin (5 g.), sulphuric acid (62° Bé; 125 g.), glycerol (10 g.), and aniline sulphate (7.5 g.) was gradually heated to 150° and kept there for 1 hour. The liquid, when poured into water, gave a green precipitate; this was dried and dissolved in alcohol and the solution was concentrated and poured into much ether. From the residue obtained by evaporation of the ether, only unchanged alizarin could be isolated. Better results were obtained by first heating the solution of alizarin and aniline sulphate at 150° for an hour, then adding the glycerol and heating again for an hour. The product, isolated with ether as above stated, gave on acetylation a small quantity of an acetyl compound, m. p. 243—245°, identical with monoacetylisobenzalizarin (mixed melting point).

*2-Acetylanthragallol Boroacetate.*—1 : 2 : 3-Trihydroxy-9-anthrone (1 g.) in cold acetic anhydride (6 c.c.) was treated with boroacetic anhydride (0.15 g.) and a few drops of pyridine, and the mixture kept over-night. The anthranol, without apparent solution, was converted into a dull orange, crystalline powder; this was collected, washed with acetic anhydride and with anhydrous ether, and centrifuged until dry. It was slowly decomposed by cold and rapidly by hot water, yielding, in addition to boric and acetic acids, 2-acetylanthragallolanthranol (m. p. 239—240°, decomp.) [Found by Dimroth's method (*loc. cit.*): 2-acetylanthragallolanthranol, 68.6, 69.8; acetic acid, 27.1, 26.4; boric acid, 13.7, 14.3.  $C_{16}H_{11}O_5B(OAc)_2$  requires 2 acetylanthragallolanthranol, 68.9; acetic acid, 29.1; boric acid, 15.05%].

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