CLXXXII.—*Reduction Products of the Hydroxyanthraquinones. Part IX.*

By Alexander Macmaster and Arthur George Perkin.

The aluminium–mercury couple, by means of which 2-mono- and 2 : 6-, 2 : 7-, and 1 : 2-di-hydroxyanthracenes were readily obtained from the corresponding hydroxyanthraquinones or their anthranols, and also anthracene from anthraquinone (Hall and Perkin, J., 1923, **123**, 2029), reduces 1-mono-, 1 : 5-di-, and 1 : 2 : 3- and 1 : 2 : 6-tri-hydroxyanthraquinones, not to the hydroxyanthracenes, but

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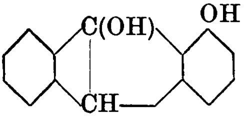
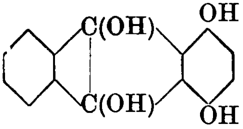
* Commercial stick. Theory requires 0·77 g. KOH for hydrolysis and methylation.

only to the hydroxyanthranols. The stability of these hydroxyanthranols is thus evidently due to the effect of one or other of the hydroxyls present therein, and these it is now known occupy the 1-, 1 : 5-, 1 : 2 : 3-, and 1 : 2 : 6-positions, respectively (Cross and Perkin, preceding paper). There is evidence that in compounds of this type a residual affinity exists between the hydroxyls in positions 1 and 9, as, for instance, in quinizarin, which is reduced by stannous chloride and hydrochloric acid merely to *leuco*-quinizarin (II) and not further to the hydroxyanthranol. The resistance of 1-hydroxyanthranol (I) to reduction by the aluminium–mercury couple also harmonises with this view, but, on the other hand, there are cases where a somewhat similar behaviour is observed with substances of this type in which the 1-hydroxyl is absent. For example, though 3 : 4-dihydroxy(alizarin)-anthranol, on treatment with the couple, readily yields 1 : 2-dihydroxyanthracene, 3 : 4 : 6-trihydroxy(anthrapurpurin)-anthranol gives but traces of a reduction product, which has not yet been isolated pure. As a means of overcoming this difficulty, a preliminary methylation of the hydroxyanthraquinones or their anthranols suggested itself; indeed Ladgozinski (*Annalen*, 1905, **342**, 104) has shown that hystazarin dimethyl ether is readily reduced to 2 : 3-dimethoxyanthracene even with zinc dust and ammonia. There should be, however, no difficulty in preparing 2 : 3-dihydroxyanthracene from hystazarin itself by the aid of the aluminium–mercury couple. The present communication deals with anthrapurpurin trimethyl ether, and this has been converted, by long digestion in alcoholic solution with the couple in presence of ammonia, into 1 : 2 : 7-trimethoxyanthracene in moderate yield. For the preparation of anthrapurpurin trimethyl ether, the method of Graebe and Bernhard (*Annalen*, 1906, **349**, 222) was employed, that is, 3 : 4 : 6-trihydroxyanthranol was methylated and then oxidised with chromic acid. The methylated anthranol, which was not closely examined by those authors, is the 3 : 4 : 6 : 9-tetramethoxy-compound, and this is interesting because the analogous product from deoxyalizarin (3 : 4-dihydroxyanthranol) is 3 : 4-dimethoxyanthrone (Graebe and Thode, *Annalen*, 1906, **349**, 207). In addition to the tetramethoxy-compound, some 3 : 4 : 6-trimethoxyanthranol was produced, a compound which is more readily obtained by the reduction of anthrapurpurin trimethyl

(I.)





(II.)

ether in acetic acid solution with stannous chloride and hydrochloric acid. This with acetic anhydride and pyridine yields the 3 : 4 : 6-trimethoxy-9-acetyl compound. Finally, if air is not excluded during the methylation process, a small amount of 3 : 4 : 6 : 3′ : 4′ : 6′-hexamethoxydianthrone is formed. This can also be prepared by the oxidation of 3 : 4 : 6-trimethoxyanthranol with ferric chloride in presence of acetic acid.

EXPERIMENTAL.

3 : 4 : 6-Trihydroxyanthranol was obtained from commercial anthrapurpurin by reduction with stannous chloride and hydrochloric acid (Goodall and Perkin, J., 1924, **125**, 470), and the acetylated product was crystallised from alcohol–acetic acid until it was free from acetyl*iso*anthraflavic acid anthranol. To a suspension of the product (10 g.) in boiling 80% methyl alcohol (300 c.c.), potassium hydroxide (50 g. in 50 c.c. of water) and methyl sulphate (55 c.c.) were slowly added through capillary tubes attached to the condenser; the mixture was kept slightly alkaline, and access of air was prevented as far as possible. The liquid, after being acidified, slowly deposited crystals, which were washed with dilute alkali solution and dried over sulphuric acid. The pale brown product (yield, 60%) was repeatedly extracted with boiling ligroin (200 c.c.). The extract after concentration deposited pale yellow needles which melted at 107° after recrystallisation (yield, 40%) (Found: C, 72·4; H, 6·0; CH_3, 20·0. $C_{18}H_{18}O_4$ requires C, 72·4; H, 6·0; CH_3, 20·0%). 3 : 4 : 6 : 9-*Tetramethoxyanthranol* gives green, fluorescent solutions, and dissolves in sulphuric acid with a brown colour which changes to purple on addition of a trace of nitric acid. That portion of the methylation product insoluble in ligroin contained, in addition to anthrapurpurin trimethyl ether, a small amount of 3 : 4 : 6-trimethoxyanthrone, a compound described later.

3 : 4 : 6 : 9-Tetramethoxyanthranol (9·5 g.) was oxidised in boiling acetic acid (65 c.c.) with a solution of chromic acid (7 g.) in acetic acid (10 c.c.) and water (15 c.c.). When cold, the anthrapurpurin trimethyl ether was collected and recrystallised from benzene. It melted at 198° (Graebe and Bernhard, *loc. cit.*, give m. p. 201°).

1 : 2 : 7-*Trimethoxyanthracene.*—A solution of anthrapurpurin trimethyl ether (4 g.) in cold sulphuric acid was poured into water, and the precipitate was collected and added in the moist condition to alcohol (100 c.c.). The suspension was boiled and treated with the aluminium–mercury couple (0·5 g.) and concentrated ammonia solution (6 c.c.), these additions being repeated five times during

4 hours. The blue, fluorescent solution, acidified with hydrochloric acid and evaporated to one-fourth of its bulk, deposited crystals (2·2 g.), which were washed with dilute alkali solution and recrystallised from ligroin (yield, 1·8 g.) (Found: C, 75·8; H, 5·9; CH_3, 16·3. $C_{17}H_{16}O_3$ requires C, 75·55; H, 5·9; CH_3, 16·7%). 1 : 2 : 7-*Trimethoxyanthracene* forms prismatic needles which melt at 95° and are very soluble in the usual solvents. Its solutions in benzene and alcohol are fluorescent. The solution in sulphuric acid is orange-yellow, but on gentle heating becomes a plum-coloured liquid with a green fluorescence, a type of colour change common to the hydroxyanthracenes (Hall and Perkin, *loc. cit.*, p. 2032).

3 : 4 : 6-*Trimethoxyanthranol.*—To a boiling solution of stannous chloride (10 g.) in hydrochloric acid (25 c.c.), anthrapurpurin trimethyl ether (1 g.), dissolved in acetic acid (30 c.c.), was added, and the digestion continued for 1 hour. The liquid, diluted with hot hydrochloric acid, deposited canary-yellow crystals, which became almost colourless after washing (yield, 0·9 g.) and were obtained in needles, m. p. 149°, by recrystallisation from alcohol (Found: C, 71·85; H, 5·5; CH_3, 15·4. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6; CH_3, 15·8%). 9-*Acetyl*-3 : 4 : 6-*trimethoxyanthranol*, obtained by acetylation in the usual manner, formed colourless needles, m. p. 127° (Found: $C_2H_4O_2$, 13·9. $C_{19}H_{18}O_5$ requires $C_2H_4O_2$, 13·2%).

3 : 4 : 6 : 3′ : 4′ : 6′-*Hexamethoxydianthrone.*—A solution of 3 : 4 : 6-trimethoxyanthranol (7 g.) in acetic acid (25 c.c.) was treated with commercial ferric chloride (10 g.) in acetic acid (10 c.c.) and gently boiled for 2 hours. When cold, the crystals were collected, washed with alcohol, and recrystallised from alcohol–acetic acid (Found: C, 72·3; H, 5·2; CH_3, 15·6. $C_{34}H_{30}O_8$ requires C, 72·1; H, 5·3; CH_3, 15·9%). The *hexamethoxy*-compound forms colourless needles which are very sparingly soluble in alcohol, melt at 224°, and dissolve in sulphuric acid with a yellow colour which becomes purple on heating. It does not appear to enolise readily and does not pass into the acetyldianthranol when digested with boiling acetic anhydride and pyridine. Attempts to convert this compound into the corresponding dianthraquinone and helianthrone have as yet been unsuccessful.

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