

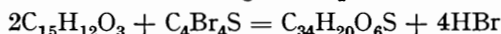
108. *Reduction Products of the Hydroxyanthraquinones. Part XV. Green Vat Dyes derived from Thiophen and 3-Substituted 4-Hydroxyanthranols.*

By (the late) ARTHUR GEORGE PERKIN and NORMAN HULTON HADDOCK.

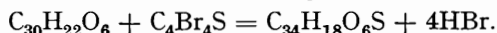
The interaction of 4-hydroxy-3-methoxyanthranol, or 4:4'-dihydroxy-3:3'-dimethoxydianthrone, and tetrachloro- or tetrabromo-thiophen, or of 3:4-dihydroxyanthranol with methyl sulphate, anhydrous sodium carbonate, and commercial tri-

chlorobenzene (containing chlorothiophens) gives a green vat dye, for which a constitution is suggested. A green dye of analogous constitution is obtained from 4-hydroxy-3-methylantranol and commercial trichlorobenzene.

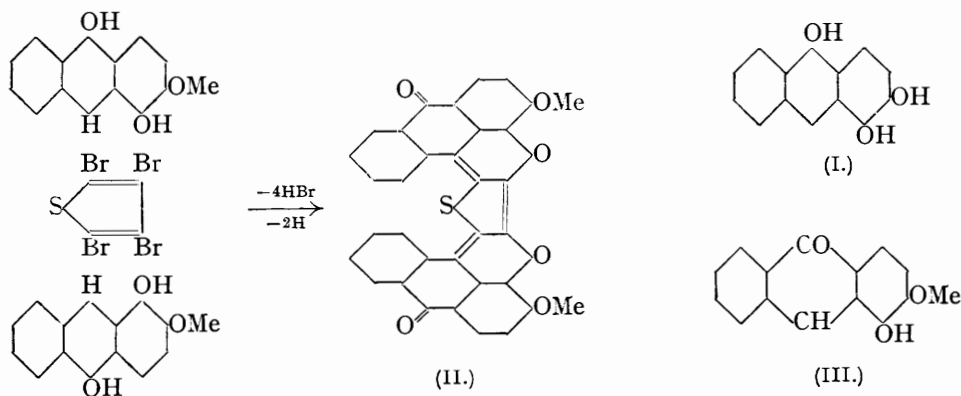
DURING experiments with the object of methylating 3 : 4-dihydroxyanthranol (I) by means of methyl sulphate and anhydrous alkali carbonate, commercial trichlorobenzene was used as a solvent. The result was unexpected, for, as heating proceeded, a dark green vat dye was progressively precipitated. It thus appeared likely that the methylated anthranol at first produced had reacted with some constituent of the crude trichlorobenzene, and such a view was confirmed by digesting 4-hydroxy-3-methoxyanthranol in this solvent, the same dye being obtained, but no reaction occurred with 3 : 4-dimethoxyanthranol. Fractions derived from this technical trichlorobenzene consisted mainly of 1 : 3 : 5-, 1 : 2 : 3-, 1 : 2 : 4-trichlorobenzenes, and 1 : 2 : 3 : 4-tetrachlorobenzene, and each reacted in this way with 4-hydroxy-3-methoxyanthranol, but the pure chloro-compounds specially prepared for this purpose gave negative results. The clue to the nature of the condensation was indicated by the presence of sulphur in the pure dye, which suggested the reactant to be a chlorothiophen, crude benzene having evidently been employed for the production of the technical trichloro-compound. The subsequent preparation from thiophen itself of tetrachlorothiophen, which with 4-hydroxy-3-methoxyanthranol in nitrobenzene solution readily yielded this green dye, undoubtedly proved it to be the reactant in question. The condensation of tetrachlorothiophen with 4-hydroxy-3-methoxyanthranol proceeded with evolution of hydrogen chloride, the dye produced being free from halogen, and indeed an identical compound was obtained when tetrabromothiophen was employed. Recrystallised from much nitrobenzene, this dye, here termed the "methoxy-green" dye, forms fine needles with a coppery lustre, insoluble in dilute alkali, and giving a blue vat with alkaline hyposulphite. The analytical results support the formula $C_{34}H_{18}O_6S$, and appear to suggest that the reaction occurs between two molecules of 4-hydroxy-3-methoxyanthranol and one molecule of the tetrahalogenothiophen, thus,



this passing by further oxidation into the colouring matter (II). Experiment has shown, however, that 4 : 4'-dihydroxy-3 : 3'-dimethoxydianthrone, which previous work has indicated is likely to be produced from the anthranol by air oxidation in the hot solvent during the digestion, reacts in these circumstances as well as, if not better than, the anthranol. Dye formation will thus occur directly :



The condensation with the anthranol can be expressed as follows :



and in a similar manner with the dianthrone the free radical (III) comes into play. Formula (II) is of interest, as it contains not only a thiophen residue, but also two pyran nuclei. Although the presence of the latter was indicated by the absence of hydroxyl groups in the dye, more certain evidence was given by the fact that, when the dye was

cautiously oxidised with chromic acid, alizarin 2-methyl ether was the main product. It is noteworthy that, although numerous preparations of the dye were made by one of us (A. G. P.), the analytical results for methoxyl were always low. It was thus evident that, under the experimental conditions employed, it was impossible to obtain a pure compound.

For the reaction with a tetrahalogenothiophen to occur, the presence in the anthranol of the 4-hydroxy-group is essential. The behaviour of 4-hydroxy- and 1:5-dihydroxy-anthranols with tetrachlorothiophen was studied, but dye formation did not occur in the latter case and only to a small extent in the former. This suggested that in the case of 4-hydroxy-3-methoxyanthranol the methoxy-group has a directing influence on the course of the reaction and does not merely enhance the chromophoric effect in the resulting dye. It was thus of interest to study the behaviour of the methyl group in this respect, and for this purpose 4-hydroxy-3-methylanthranol, readily prepared from 1-acetoxy-2-methyl-anthraquinone by the method of Cross and Perkin (J., 1930, 292), was employed. From this, by digestion with technical trichlorobenzene, a dye, similar in character to the "methoxy-green" discussed above, was produced in almost theoretical yield; it is here distinguished as the "methyl-green" dye. The "methyl-green" dye, which was obtained as a coppery mass of fine flat needles, gave analyses corresponding with the formula $C_{34}H_{18}O_4S$, and can be represented in the same manner as (II) by replacing the two methoxy-groups by methyl groups. When it was oxidised gently with chromic acid, the main product was 1-hydroxy-2-methylanthraquinone, together with a little of a substance, greenish prisms, m. p. 300—303°, having apparently the formula $C_{34}H_{18}O_6S$, and traces of a substance, orange-yellow needles, m. p. 303—305°, which from the analytical data, m. p. and mixed m. p., and other properties, appeared to be either a modification of the former substance or to be closely related to it. In addition to alizarin 2-methyl ether, a trace of a similar yellow substance was isolated from the oxidation mixture of the "methoxy-green" dye.

Both dyes, the "methoxy-green" and the "methyl-green," dye cotton from a hypsulphite vat deep shades of considerable beauty and of a fairly permanent character, but these are less fast to light and hypochlorite solution than other well-known green vat dyes now on the market. Otherwise, owing to the simplicity of their methods of preparation, these new dyes would possess considerable technical importance. The process of manufacture of the "methoxy-green" dye is covered in B.P. 353,422, granted to Imperial Chemical Industries, Ltd., A. G. Perkin, A. Shepherdson, and N. H. Haddock.

EXPERIMENTAL.

4-Hydroxy-3-methoxyanthranol.—A modification of the method of Cross and Perkin (J., 1930, 292) was employed. Acetyl alizarin 2-methyl ether (20 g.) in boiling glacial acetic acid (200 c.c.) was cooled to 90°, stannous chloride-hydrochloric acid (200 c.c. of a solution of 400 g. of stannous chloride in 1 l. of hydrochloric acid) added, and, after shaking, the mixture kept for 2 days. The deposit of 4-hydroxy-3-methoxyanthranol, m. p. 198—201°, was collected and washed (yield, 13.7 g.; 85%). The m. p. was raised to 203—204° by crystallisation from benzene. The acid stannous chloride filtrate on dilution gave mainly 1-hydroxy-2-methoxy-anthranol.

Tetrachlorothiophen.—Crude benzene (2 l.) was treated with bromine (120 g.) (cf. Meyer and Stadler, *Ber.*, 1885, 18, 1489), and the nearly pure dibromothiophen (30 g.), b. p. 203—207°, isolated by the method of these authors. From this, by the action of excess of chlorine below 30° (Weitz, *Ber.*, 1884, 17, 795), the tetrachloro-compound was obtained; after recrystallisation it melted at 38° (Weitz gives 36°).

Tetrabromothiophen.—Tetrabromothiophen was prepared from thiophen by direct bromination and melted at 116° (Meyer and Kreis, *Ber.*, 1883, 16, 2172, give m. p. 112°).

The "Methoxy-green" Dye.—(a) A mixture of 3:4-dihydroxyanthranol (20 g.), commercial trichlorobenzene (400 c.c.), anhydrous sodium carbonate (30 g.), and methyl sulphate (30 g.) was well stirred and heated at 190—200° for 3 hours. The green precipitate was collected and washed with water (yield, 7.5 g.). Longer digestion (4 hours) gave an increased yield (19.9 g.) of a less pure substance. On account of its sparing solubility in nitrobenzene, the product was suspended in a calico bag under reflux and extracted with the boiling solvent for 24 hours. The crystals were collected and washed with alcohol (yield, 10 g.).

544 Reduction Products of the Hydroxyanthraquinones. Part XV.

(b) 4-Hydroxy-3-methoxyanthranol (1 g.) and tetrachlorothiophen (1 g.) were dissolved in hot naphthalene, the mixture boiled for 5 hours, and the dye isolated by means of hot benzene (yield, 0.7 g.) (Found: C, 73.0; H, 3.4; S, 5.5; OMe, 9.2. $C_{34}H_{18}O_8S$ requires C, 73.6; H, 3.3; S, 5.75; OMe, 11.1%). By a similar procedure with tetrabromothiophen (2 g.), an analogous result was obtained (Found: C, 73.4; H, 3.5; S, 6.3; OMe, 8.15%).

(c) 4:4'-Dihydroxy-3:3'-dimethoxydianthrone (0.2 g.), anhydrous sodium carbonate (0.3 g.) and commercial trichlorobenzene (3 c.c.) were stirred together and heated at 190—195° for 3 hours. The green precipitate (0.15 g.) was collected and washed with alcohol and finally with water. The product was identical in reactions with those obtained under (a) and (b).

Oxidation of the "Methoxy-green" Dye.—The "methoxy-green" dye (5 g.) was ground into a paste with glacial acetic acid, the suspension diluted to 75 c.c. and heated to 75°, and a solution of chromic acid (3.5 g.) in acetic acid (32 c.c.) and water (3 c.c.) added in portions (5 c.c.) during 45 minutes, the temperature being kept almost constant throughout and for a further 15 minutes. After 12 hours, the residue (A) (2.8 g.) was collected. The filtrate was diluted with water and gave a dull orange-brown powder (0.8 g.). The latter was extracted with boiling benzene and filtered (charcoal), benzene removed from the filtrate, the residue dissolved in alcohol, and the solution concentrated. The orange-red product was acetylated in presence of pyridine for 1 hour, and the liquid (charcoal) filtered and diluted with alcohol. Recrystallisation of the product from alcohol-acetic acid gave acetyl alizarin 2-methyl ether in pale yellow needles, m. p. 203—205° (Found: C, 69.1; H, 4.0. Calc. for $C_{17}H_{12}O_5$: C, 69.5; H, 4.1%). This was converted by hydrolysis with hydrochloric acid into alizarin 2-methyl ether, orange-red needles, m. p. 228—230° (Found: C, 70.9; H, 4.0. Calc. for $C_{15}H_{10}O_4$: C, 71.2; H, 4.0%).

The residue (A) consisted mainly of unattacked "methoxy-green" dye, but after digestion with much boiling glacial acetic acid the extract deposited a small amount of fine yellow crystals. These dissolved in boiling pyridine, and on addition of alcohol separated in a purer condition, but in too small amount for examination.

1-Hydroxy-2-methylanthraquinone.—This compound, obtained by Bentley, Gardner, and Weizmann (J., 1907, 91, 1635) from *o*-cresol and phthalic anhydride, was prepared from 1-amino-2-methylanthraquinone (100 g.) in sulphuric acid (1000 g.) by gradual diazotisation with sodium nitrite (33 g.) at room temperature, and decomposition of the product by addition of water (5%) and heating at 90° for 5 hours. On dilution with much water, crude 1-hydroxy-2-methylanthraquinone, m. p. 178—180°, separated (yield, 94.5%). After purification *via* the acetyl compound, the m. p. was 184° (cf. Bentley, Gardner, and Weizmann, *loc. cit.*).

1-Acetoxy-2-methylanthraquinone, prepared in the usual manner, crystallised in pale yellow needles, m. p. 187—189° (Found: C, 72.6; H, 4.5. $C_{17}H_{12}O_4$ requires C, 72.8; H, 4.3%).

4-Hydroxy-3-methylanthrone.—To the above acetoxy-compound (10 g.) in glacial acetic acid (100 c.c.) at 90°, stannous chloride (30 g.) in hydrochloric acid (70 c.c.) was added. After 2 days, the product, almost colourless needles, m. p. 197°, was collected (yield, 92.6%).

The "Methyl-green" Dye.—A solution of 4-hydroxy-3-methylanthrone (10 g.) in commercial trichlorobenzene (100 c.c.) (containing 3.36% of sulphur, equivalent to 8.8% of thiophen), which at 170° gave evidence of dye formation, was boiled (195°) for 5 hours. The collected product was washed with alcohol (yield, 5.4 g.). When a larger volume of commercial trichlorobenzene (260 c.c.) was used with addition of potassium acetate (10 g.), the yield was increased (11.08 g.). The "methyl-green" dye was recrystallised from much nitrobenzene, in which it is more soluble than the "methoxy-green" dye (Found: C, 77.7; H, 3.6; S, 6.1. $C_{34}H_{18}O_8S$ requires C, 78.1; H, 3.5; S, 6.1%. $C_{34}H_{20}O_8S$ requires C, 77.9; H, 3.8; S, 6.1%).

Oxidation of the "Methyl-green" Dye.—The "methyl-green" dye (3 g.) was ground into a cream with glacial acetic acid (45 c.c.) and a solution of chromic acid (2.5 g.) in glacial acetic acid (30 c.c.) containing a little water was gradually added during 1 hour at 70°. After keeping overnight, the residue (A) (1.05 g.) was collected. The filtrate was diluted with water and gave a dull orange product (1.25 g.), which was extracted with benzene (charcoal) and filtered, and benzene removed from the filtrate. The resulting residue was boiled with much alcohol; a little red powder (B) (0.05 g. approx.) was then deposited. The alcoholic filtrate on concentration gave crystals, converted by acetylation and recrystallisation from alcohol-acetic acid into 1-acetoxy-2-methylanthraquinone, pale yellow needles, m. p. 187—189°, hydrolysed to 1-hydroxy-2-methylanthraquinone, m. p. 184—185° (Found: C, 75.6; H, 4.3. Calc. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.2%).

Residue (B), after two crystallisations from benzene, consisted of small greenish prisms,

m. p. 300—303° (Found : C, 73·5; H, 3·45; S, 5·4. $C_{34}H_{18}O_6S$ requires C, 73·6; H, 3·3; S, 5·7%), insoluble in alkalis, but soluble in sulphuric acid with a dull red tint, becoming green at the edges on keeping. The residue (A) was extracted with a large amount of boiling benzene and left much "methyl-green" dye undissolved. The extract (charcoal) on concentration gave orange-yellow needles, which after recrystallisation melted at 303—305° (C) (Found : C, 73·5; H, 3·4; S, 5·4. $C_{34}H_{18}O_6S$ requires C, 73·6; H, 3·3; S, 5·7%), and dissolved in sulphuric acid with a dull red tint, becoming green at the edges; it gave with alkaline hypsulphite a yellow liquid and had similar properties to (B). The mixed m. p. of (B) and (C) was 300°, and possibly (B) is slightly impure (C), or a modification of it.

The authors acknowledge gifts of material from Imperial Chemical Industries, Ltd., and the help given by Mr. W. W. Tatum (of Imperial Chemical Industries, Ltd., Dyestuffs Group), who prepared the "methyl-green" dye, and by Mr. C. Hollins (of Imperial Chemical Industries, Ltd.), who suggested that the reactant in technical trichlorobenzene was a chlorinated thiophen. One of the authors (N. H. H.) desires to thank Imperial Chemical Industries, Ltd., for permission to publish this paper.

THE UNIVERSITY, LEEDS.
RESEARCH LABORATORIES, BLACKLEY.

[Received, February 15th, 1938.]
