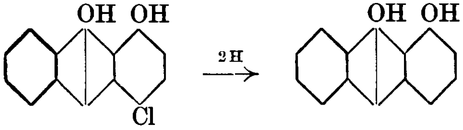
CCCXIII.—*The Determination of the Structure of α-Hydroxyanthranols.*

By Albert Green.

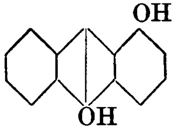
The reduction of an α-hydroxyanthraquinone to the corresponding anthranol may occur in two ways: *e.g.*, 1-hydroxyanthraquinone may give 1 : 9-dihydroxyanthracene (I), 1 : 10-dihydroxyanthracene (II), or a mixture of these two.

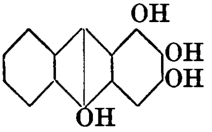
(III.)



(I.)

(II.)





(IV.)

By the reduction of alizarin 2-methyl ether, Miller and Perkin (J., 1925, **127**, 2684) obtained a mixture of the two possible isomeric anthranols, and were able to assign structures to them by observing the differences in the resistance of the derived benzanthrones to methylation. The use of the benzanthrone condensation in the determination of the structures of reactive substances such as the anthranols has disadvantages: purification of the products is tedious, and the yields are very small. Miller and Perkin (*loc. cit.*) themselves suggest that the poor yields are a result of the anthranols suffering alteration during heating with sulphuric acid for 1 hour at 125—130°. However, in a later paper (Cross and Perkin, this vol., p. 1297) improved methods of effecting the benzanthrone condensation are described.

The present method for deciding whether an anthranol is of type (I) or of type (II) depends on its reaction with thionyl chloride, which takes place at the ordinary temperature. It has been shown (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554) that two *ortho*-hydroxyl groups of a phenol always react with thionyl chloride to give a thionyl derivative, but that a similar compound is not given by *meta-* or *para*-dihydric phenols (J., 1926, 1428; this vol., p. 500). In view of the well-established resemblance between reactions shown by certain substituents in the *peri*-position (I) and those of the same groups in the *ortho*-position, it was anticipated that a compound of type (I) would yield a thionyl derivative, whereas one of type (II) would not.

These anticipations were verified by examining, in the first place, the action of thionyl chloride on two substances of known structure, 1 : 8- and 1 : 5-dihydroxynaphthalene. When the former, in carbon disulphide–pyridine solution, is treated with the theoretical quantity of thionyl chloride it gives 1 : 8-*thionyldihydroxynaphthalene* in quantitative yield. The isomeric 1 : 5-dihydroxy-compound, on the contrary, does not give a thionyl derivative : all the methods of preparation previously described (*loc. cit.*) were used, and in every case the products were complex mixtures which always contained chlorine.

The method was then applied to three anthranols. Two of these, 1-hydroxyanthranol and 4-*chloro*-1-*hydroxyanthranol,* yield thionyl derivatives, and are therefore 1 : 9-dihydroxyanthracene (I) and 4-*chloro*-1 : 9-*dihydroxyanthracene* (III) respectively. In preparing the latter by reduction of 4-chloro-1-hydroxyanthraquinone, it was necessary to avoid over-reduction, which readily led to the replacement of the chlorine atom by hydrogen, with production of 1 : 9-dihydroxyanthracene (I).

The products of four experiments with anthragallol anthranol and thionyl chloride were all complex chlorine-containing mixtures, thus indicating that this anthranol is not 1 : 2 : 3 : 9-tetrahydroxyanthracene—for this would be expected to give a chlorine-free dithionyl derivative, since anthragallol itself yields 2 : 3-thionylanthragallol (J., 1926, 2202)—but is 1 : 2 : 3 : 10-tetrahydroxyanthracene (IV). This conclusion, which is based on negative evidence only, is contrary to that reached by Cross and Perkin (*loc. cit.*).

The anthranols used in this investigation were prepared from the corresponding anthraquinones by the method of Liebermann and Mamlock (*Ber.*, 1905, **38**, 1795), with tin and hydrochloric acid in acetic acid solution as reducing agent. This method was preferred to the more economical one of Breare and Perkin (J., 1923, **123**, 2606), who used a hydrochloric acid solution of stannous chloride, because the products were more easily purified.

The compounds described herein differ from the thionyl derivatives examined previously (*loc. cit.*) in that the thionyl group forms part of a six-atom ring, and is less reactive than one forming part of a heterocyclic structure of five atoms.

EXPERIMENTAL.

Preparation of Materials.—1 : 8-*Dihydroxynaphthalene.* A commercial specimen labelled "pure" contained more than 70% of impurities. The naphthol was eventually obtained pure by two methods : (I) A hot solution of the mixture in acetic anhydride and pyridine, on cooling, deposited practically pure 1 : 8-diacetoxynaphthalene. After one recrystallisation from acetic anhydride, this formed small, white plates of constant m. p. 155° (Erdmann, *Annalen*, 1888, **247**, 359, gives 147—148°) (Found: $CH_3{\cdot}CO$, 35·7. Calc.: 35·3%). The acetyl derivative was hydrolysed by the rapid addition of hydrochloric acid to its solution in hot acetic acid. After removal of some tarry matter by filtration through asbestos, a warm saturated solution of sulphur dioxide was added, and 1 : 8-dihydroxynaphthalene separated as hair-like, white needles, m. p. 144° (Found: C, 74·8; H, 5·1. Calc.: C, 75·0; H, 5·0%). (II) The impurities were very sparingly soluble in cold acetic acid, and were removed by fractional crystallisation. The acetic acid solutions, when diluted with water, yielded the naphthol as small, greyish-white crystals, which, after drying over sulphuric acid, melted at 142—143° (Found: C, 74·8; H, 5·2%). 1 : 8-Dihydroxynaphthalene dissolves in concentrated sulphuric acid with a greenish-gold colour, and its colourless solution in alcohol becomes dark green on the addition of ferric chloride.

The anthraquinones, which were converted into the anthranols, were obtained by the hydrolysis of the purified acetyl derivatives (compare J., 1926, 1431, 2199).

1 : 9-*Dihydroxyanthracene* (1-*Hydroxyanthranol*). This was obtained, by treating the hot acetic acid solution of the diacetate with hydrochloric acid, as faintly yellow, square plates, m. p. 142° (Found: C, 79·9; H, 4·9. Calc.: C, 80·0; H, 4·8%). The diacetate separated from a mixture of acetic anhydride and pyridine in short, pale yellow, six-sided prisms, m. p. 211° (Found: $CH_3{\cdot}CO$, 29·3. Calc.: $CH_3{\cdot}CO$, 29·3%).

4-*Chloro*-1 : 9-*dihydroxyanthracene* (4-*Chloro*-1-*hydroxyanthranol*). Owing to the ease with which 4-chloro-1-hydroxyanthraquinone was reduced to 1 : 9-dihydroxyanthracene, it was necessary to control the reduction carefully. The addition of hydrochloric acid to the acetic acid solution was stopped as soon as a test portion, added to excess of caustic soda, no longer showed a trace of the red colour of the sodium salt of the hydroxyanthraquinone (about 3 minutes). The solution was then rapidly decanted from the residual tin and cooled. The acetylated product, after recrystallisation from absolute alcohol, yielded 4-*chloro*-1 : 9-*diacetoxyanthracene* as rosettes of faintly yellow, fine needles, m. p. 157° [Found: Cl, 10·7; $CH_3{\cdot}CO$, 28·5. $C_{14}H_7O_2Cl(CH_3{\cdot}CO)_2$ requires Cl, 10·8; $CH_3{\cdot}CO$, 28·2%]. The hot acetic acid solution of these, when treated with hydrochloric acid, deposited 4-*chloro*-1 : 9-*dihydroxyanthracene* as pale greenish-yellow needles of constant m. p. 170—171° (Found: Cl, 14·5; *M*, cryoscopic in naphthalene, 245, 250. $C_{14}H_9O_2Cl$ requires Cl, 14·5%; *M*, 244·5), giving a bright greenish-gold solution in concentrated sulphuric acid. Its solution in aqueous caustic soda is bright yellow, but on standing in air this is rapidly oxidised to the wine-red solution characteristic of the sodium salt of 4-chloro-1-hydroxyanthraquinone. In alcohol, the anthranol gives a pale greenish-yellow solution which becomes golden-brown on the addition of ferric chloride.

When 3·2 g. of 4-chloro-1 : 9-dihydroxyanthracene were reduced further by the method of Liebermann and Mamlock (*loc. cit.*) during 40 minutes, the product contained less than 1% of chlorine. Its solution in a mixture of warm pyridine and acetic anhydride deposited 2·1 g. of 1 : 9-diacetoxyanthracene, m. p. 208—209°, which after one recrystallisation from the same mixture melted at 210—211°, either alone or mixed with an authentic specimen (Found : $CH_3 \cdot CO$, 29·6. Calc. : 29·3%).

The thionyl derivatives were prepared by the method adopted for 1 : 2-thionyldihydroxyanthracene (this vol., p. 557).

1 : 8-*Thionyldihydroxynaphthalene* (5·5 g. from 5·3 g. of the naphthol) separated from carbon disulphide in small, pearl-grey crystals, m. p. 97° (Found : C, 58·6 ; H, 2·9 ; S, 15·5 ; *M*, cryoscopic in naphthalene, 218, 210. $C_{10}H_6O_3S$ requires C, 58·3 ; H, 2·9 ; S, 15·5% ; *M*, 206). It is stable to moisture and a specimen which had stood in air for 9 weeks showed no change in m. p. or in sulphur content. Cold aqueous caustic potash has no appreciable effect on the thionyl compound, but a hot alcoholic solution decomposes it with the production of a pale amethyst colour and the deposition of potassium sulphite. The thionyl compound dissolves in concentrated sulphuric acid with a dull amethyst colour, which changes to the greenish-gold of the naphthol when the solution is heated.

1 : 9-*Thionyldihydroxyanthracene* was obtained (5·0 g. from 4·8 g. of anthranol) from carbon disulphide as pale greenish-yellow plates, m. p. 115° (decomp.) (Found : C, 65·7 ; H, 3·2 ; S, 12·7 ; *M*, cryoscopic in naphthalene, 260, 264. $C_{14}H_8O_3S$ requires C, 65·6 ; H, 3·1 ; S, 12·5% ; *M*, 256). It gives a greenish-gold solution in cold concentrated sulphuric acid ; it is not appreciably soluble in cold caustic soda, but yields a light golden-brown solution on warming. The addition of ferric chloride to its pale yellow solution in alcohol produces no change.

4-*Chloro*-1 : 9-*thionyldihydroxyanthracene* crystallised from carbon disulphide in pale greenish-yellow plates, m. p. 123—124° (decomp.), 4·0 g. of anthranol yielding the same amount of thionyl derivative (Found : S, 11·2 ; Cl, 12·0 ; *M*, cryoscopic in naphthalene, 295. $C_{14}H_7O_3ClS$ requires S, 11·0 ; Cl, 12·2% ; *M*, 290·5). The colour reactions are similar to those of 1 : 9-thionyldihydroxyanthracene.

The products obtained by treating 1 : 5-dihydroxynaphthalene with thionyl chloride showed chlorine contents varying from 14 to 22%; those from anthragallol anthranol contained sulphur in amounts varying from 0·7 to 15·6%, and chlorine from 2·1 to 21·5%. In all cases, the reactions and properties of the products pointed to their being complex substances formed by the condensation of several molecules.

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