LXXXIII.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part II. 1 : 2- and 2 : 3-Thionyldihydroxyanthracenes.*

By ALBERT GREEN.

PHENOLIC thionyl derivatives have been classified (this vol., p. 500) according to their behaviour with weak organic acids. In the present paper, the thionyl derivatives of dihydroxyanthracenes are compared with those of the corresponding dihydroxyanthraquinones (J., 1924, **125**, 1450; 1926, 2198).

1 : 2-Dihydroxyanthracene is obtainable from 1 : 2-dihydroxyanthranol (deoxyalizarin) by Perkin's reduction method (J., 1923, **123**, 2029).

2 : 3-Dihydroxyanthracene has been described, as straw-yellow plates darkening at 180° and melting at about 192°, by Lagodinski (*Annalen*, 1905, **342**, 106), who obtained it by boiling its dimethyl ether with hydriodic acid. The diacetyl derivative melted at 155—160°. The present author prepared 2 : 3-dihydroxyanthracene from hystazarin by the two-stage reduction method (stannous chloride followed by the aluminium–mercury couple) used by Perkin (*loc. cit.*, pp. 2029, 2606) in the preparation of other hydroxyanthracenes from the hydroxyanthraquinones. The properties of the intermediate anthranol so obtained agreed with those ascribed to it by Schrobsdorff (*Ber.*, 1903, **36**, 2938), who reduced hystazarin by means of zinc dust and ammonia. 2 : 3-Dihydroxyanthranol, on reduction by the couple, gave a product, m. p. 282°, whose diacetyl derivative melted at 175°. These properties do not agree with those of Lagodinski's substance, but confirmation of the new product as 2 : 3-dihydroxyanthracene was obtained by analyses, by molecular-weight determinations, and by the oxidation of the acetyl derivative to diacetylhystazarin. The colour reactions of the compound described herein conform substantially with those of Lagodinski's substance, and the probability of the latter having

been obtained in a very impure state is supported by the indefinite melting point and the yellow colour ascribed to the acetyl derivative.

Unfortunately, all attempts to prepare the dimethyl ether from 2 : 3-dihydroxyanthracene were fruitless, although methyl sulphate, diazomethane, and hydrolysis of the diacetyl derivative by sulphuric acid and by hydrogen chloride in absolute methyl-alcoholic solution were resorted to. Similar resistance of other dihydroxyanthracenes to etherification has been noted by Perkin (*loc. cit.*, p. 2035). Lagodinski prepared his 2 : 3-dimethoxyanthracene from veratrole and phthalic anhydride through *o*-3′ : 4′-dimethoxybenzoylbenzoic acid.

1 : 2- and 2 : 3-*Thionyldihydroxyanthracenes* were obtained by the interaction of the hydroxy-compounds and thionyl chloride in pyridine–carbon disulphide solution. They are remarkably stable to moisture, remaining unchanged after 6 weeks' contact with moist air; thionylalizarin (*loc. cit.*) completely reverts to alizarin on standing in air over-night. Both thionyl compounds are decomposed to the dihydroxyanthracenes by solution in cold concentrated sulphuric acid or in cold aqueous caustic alkali.

1 : 2-Thionyldihydroxyanthracene shows no signs of reacting with acetic acid until this boils; complex decomposition then occurs and sulphur and sulphur dioxide are produced. This unexpectedly complex reaction may be accounted for by the proximity of the reaction temperature to the m. p. of the thionyl compound, which darkens at 125° and melts at 138—139° (decomp.). A similar reaction occurs when it is heated with acetic acid and pyridine.

2 : 3-Thionyldihydroxyanthracene differs from thionylhystazarin (*loc. cit.*) in not reacting with boiling acetic acid. When a trace of pyridine is added to the solution, decomposition proceeds slowly with evolution of sulphur dioxide and formation of 2 : 3-dihydroxyanthracene. This " hydroxylic decomposition " corresponds with that of thionylhystazarin. 2 : 3-Thionyldihydroxyanthracene is quantitatively converted into 2 : 3-diacetoxyanthracene by acetic anhydride and pyridine.

EXPERIMENTAL.

1 . 2-*Dihydroxyanthracene*.—The crude reduction product from deoxyalizarin was acetylated, and the purified diacetyl derivative was hydrolysed in small quantities (1 to 2 g.) by means of acetic and hydrochloric acids (Perkin, *loc. cit.*). This tedious process appears to provide the best means of obtaining pure 1 : 2-dihydroxyanthracene in faintly green plates, m. p. 160—161° (Found : C, 79·8; H, 4·9. Calc. : C, 80·0; H, 4·8%).

2 : 3-*Dihydroxyanthracene.*—Hystazarin was recovered practically unchanged after attempts to reduce it directly to 2 : 3-dihydroxyanthracene by the aluminium–mercury couple, alcohol and ammonia.

(a) 2 : 3-*Dihydroxyanthranol.* Finely-divided, moist hystazarin, obtained by hydrolysis of its pure diacetate (compare J., 1926, 2199) with sulphuric acid, when boiled with a hydrochloric acid solution of stannous chloride until a test portion, dissolved in excess of caustic soda, showed a light greenish-yellow colour, gave a quantitative yield of the anthranol, which crystallised from alcohol in bunches of small, yellowish-brown rods, m. p. 288—289° (Schrobsdorff, *loc. cit.*, gives m. p. 282°) (Found : C, 74·2; H, 4·4. Calc. : C, 74·3; H, 4·4%). Its aqueous and alcoholic solutions give an olive-green colour with ferric chloride, and the other colour reactions correspond with those described by Schrobsdorff.

The triacetyl derivative, prepared by means of acetic anhydride and pyridine, formed white, hair-like needles (from alcohol), m. p. 164° (Found : CH_3·CO, 36·8. Calc. : CH_3·CO, 36·6%).

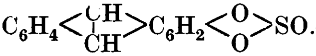
(b) 2 : 3-*Dihydroxyanthracene.* The crude damp anthranol was suspended in a mixture of water and alcohol and reduced by the aluminium–mercury couple. No tar formed, and when the mixture was stirred into dilute hydrochloric acid the hydroxyanthracene was precipitated, in theoretical yield, as a pale buff solid.

2 : 3-*Diacetoxyanthracene* was prepared by boiling this solid with acetic anhydride and pyridine; after one recrystallisation from rectified spirit, it formed white, elongated, hexagonal plates of constant m. p. 175° [Found : C, 73·4; H, 4·8; CH_3·CO, 29·5; *M*, cryoscopic in naphthalene, 286, 290. $C_{14}H_8O_2(CO{\cdot}CH_3)_2$ requires C, 73·5; H, 4·8; CH_3·CO, 29·3%; *M*, 294].

2 : 3-*Dihydroxyanthracene* was obtained pure by hydrolysing the acetyl derivative with a mixture of acetic and hydrochloric acids. It separated as faintly greenish-yellow plates, which began to sublime at about 260° and melted at 282° (Found : C, 79·9; H, 4·8; *M*, cryoscopic in naphthalene, 212, 204. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%; *M*, 210).

2 : 3-Dihydroxyanthracene dissolves in concentrated sulphuric acid with a bright golden-brown colour, and in aqueous caustic soda and in ammonia to pale green solutions. Its solutions in alcohol and in acetone are very light yellow and show a faint purple fluorescence; addition of ferric chloride to these produces a dark bluish-green colour.

(c) *Oxidation of* 2 : 3-*diacetoxyanthracene.* A boiling solution of 1 g. of 2 : 3-diacetoxyanthracene in 8 c.c. of glacial acetic acid was carefully treated with 1·6 g. of chromic anhydride dissolved in a mixture of 1·5 c.c. of water and 3 c.c. of acetic acid. After boiling for 10 minutes, the solution was stirred into water. The precipitate, after drying at 100° (1·1 g.), melted at 206—209°, and, after recrystallisation from pyridine, at 211—213°, either alone or when mixed with authentic diacetylhystazarin (Found : C, 66·5; H, 3·7; $CH_3{\cdot}CO$, 26·4. Calc. : C, 66·7; H, 3·7; $CH_3{\cdot}CO$, 26·6%).

1 : 2-*Thionyldihydroxyanthracene*,  $C_6H_4<\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_2<\genfrac{}{}{0pt}{}{O}{O}>SO$.—An excess of cold thionyl chloride reacted very vigorously with 1 : 2-dihydroxyanthracene, but the product did not yield the required thionyl derivative. This was obtained by adding 2·10 c.c. (1 mol.) of freshly-distilled thionyl chloride in 30 c.c. of dry carbon disulphide to a cold solution of 5·85 g. (1 mol.) of 1 : 2-dihydroxyanthracene in a mixture of 4·40 g. (2 mols.) of pyridine and 200 c.c. of dry carbon disulphide. The mixture was boiled on the water-bath for 20 minutes, and the hot disulphide solution was then decanted from the viscous pyridine hydrochloride and concentrated to 50 c.c. The residue in the flask was extracted with a further 200 c.c. of dry carbon disulphide, and this solution also was concentrated. From the two solutions, 4·8 g. of small, pale brown crystals separated. These darkened at about 125° and melted at 138—139° (decomp.) (Found: C, 65·4; H, 3·2; S, 12·6; *M*, cryoscopic in naphthalene, 254, 250. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1; S, 12·5%; *M*, 256).

1 : 2-*Thionyldihydroxyanthracene* dissolves in cold concentrated sulphuric acid with a transient dark orange colour which rapidly passes to royal-blue; on dilution with water, 2 : 3-dihydroxyanthracene separates. Its solution in cold aqueous caustic soda is light orange-yellow, and when acidified deposits the dihydroxy-compound. The thionyl compound dissolves in cold alcohol to a dark orange solution on which ferric chloride has no apparent effect.

Two finely powdered specimens, after standing in the air for 6 weeks, had their original weights and m. p. and sulphur contents of 12·6 and 12·5%, respectively.

2 : 3-*Thionyldihydroxyanthracene* was obtained in a similar manner to the 1 : 2-compound, 4·50 g. of the dihydroxyanthracene yielding 3·4 g. of the thionyl derivative. This separated from carbon disulphide in thin, faintly yellow flakes, which darkened at 180° and melted at 188° (decomp.) (Found: C, 65·5; H, 3·1; S, 12·6%; *M*, in freezing naphthalene, 260, 264). After standing in air for 6 weeks, a finely-ground specimen had its original weight and m. p. and a sulphur content of 12·6%.

2 : 3-*Thionyldihydroxyanthracene* gives a bright golden-brown solution in cold concentrated sulphuric acid, and a pale yellowish-

green one in cold aqueous caustic soda. These solutions, when respectively diluted with water and acidified, deposit 2 : 3-dihydroxyanthracene. The thionyl compound is very sparingly soluble in hot alcohol, and the very pale yellow solution changes to dark greenish-yellow on addition of ferric chloride.

Action of acetic acid. When 1·1 g. of 2 : 3-thionyldihydroxyanthracene were added to 15 c.c. of boiling glacial acetic acid, very little dissolved and there was no detectable evolution of sulphur dioxide. The addition of two drops of pyridine, however, caused solution to occur with elimination of sulphur dioxide. After boiling for 2 hours, the solution was stirred into cold water; it then deposited 0·9 g. of a dull yellow precipitate, which was filtered off. In order to remove any mechanically-held acetic acid, the moist product was dissolved in hot alcohol, again precipitated with water, filtered off, and thoroughly washed. It was dried over sulphuric acid and examined quantitatively for the acetyl radical, which was absent. A hot acetic acid solution of the remainder of the product, on careful dilution with a warm aqueous solution of sulphur dioxide, deposited 2 : 3-dihydroxyanthracene in pale greenish-yellow plates; these melted at 280—282°, either alone or mixed with the pure compound (Found: C, 79·8; H, 4·9. Calc.: C, 80·0; H, 4·8%).

Action of acetic anhydride. A solution of 0·6 g. of 2 : 3-thionyldihydroxyanthracene in 8 c.c. of boiling acetic anhydride showed no signs of reaction until 1 drop of pyridine was added; sulphur dioxide was then detected. The solution was cooled after 1 hour, and diluted with alcohol; it deposited 0·3 g. of hexagonal plates of 2 : 3-diacetoxyanthracene, which, alone or mixed with an authentic specimen, melted at 175°. The filtrate, when stirred into water, yielded a further 0·4 g. of the same product (Found: CH_3·CO, 29·5. Calc.: CH_3·CO, 29·3%).

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed a portion of the expenses of this research, and also The British Alizarine Company, Limited, and I.G. Farbenindustrie Aktiengesellschaft, Leverkusen, for gifts of materials.

THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.
[*Received, January 29th,* 1927.]