CCXCI.—*The Action of Thionyl Chloride on Hydroxyanthraquinones. Part III.*

By ALBERT GREEN.

WHEN purpurin is treated with boiling thionyl chloride, two only of the three hydroxyl groups enter into reaction. The product contains one sulphite group, closely resembles thionylalizarin (J., 1924, **125**, 1450) in properties, and yields 2-acetylpurpurin when boiled with acetic acid. It is therefore 1 : 2-*thionylpurpurin* (I), and, like the alizarin analogue, it reacts rapidly with moisture, reverting to the hydroxy-compound.

In the case of anthrapurpurin all three hydroxyls are affected and 1 : 2-*thionyl*-7-*chlorothionylanthrapurpurin* (II) results. This is even less stable to moisture than the previously described compounds of this series, and is converted by acetic and benzoic acids into *monoacyl* derivatives, which, in view of the analogous formation of 2-monoacetyl derivatives of alizarin and of purpurin, must be formulated as 2-acyl-1 : 7-dihydroxyanthraquinones. With acetic anhydride, the chlorothionyl compound is quickly converted into triacetylanthrapurpurin.

The thionyl derivatives of hystazarin and anthragallol are differentiated from those above mentioned by their greater stability to moisture and by their different behaviour with acetic acid. These differences must be ascribed to the different positions of the sulphite groups. When boiled with acetic acid, *thionylhystazarin* (III) reverts completely to hystazarin, whilst 2 : 3-*thionylanthragallol* (IV) gives a mixture of anthragallol and a *monoacetylanthragallol*, which from considerations of steric hindrance is probably 3-*acetylanthragallol*.

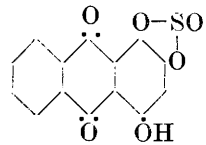
Thionylhystazarin also differs from the other thionyl derivatives of this series in that its conversion into diacetylhystazarin takes place with comparative slowness and is still uncompleted after its solution in acetic anhydride has been boiled for ½ hour.

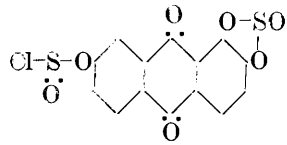
The structure of 2 : 3-thionylanthragallol is established on the evidence of its regulated interaction with acetic anhydride. Thionyl-

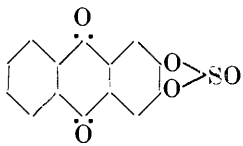
alizarin (*loc. cit.*) is quantitatively converted into diacetyl-alizarin by boiling its solution in acetic anhydride for 10 minutes; furthermore, Dimroth, Friedman, and Kammerer (*Ber.*, 1920, **53**, 481) have shown that 1-hydroxyl groups are scarcely affected when hydroxyanthraquinones are boiled with the anhydride for this time. When thionylanthragallol is so treated, a theoretical yield of 2 : 3-diacetylanthragallol results, and it is thus clear that the thionyl group is not linked to the 1-position of the anthragallol nucleus.

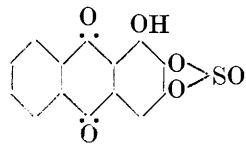
Anthraquinone, 1-hydroxyanthraquinone, 4- and 5-chloro-1-hydroxyanthraquinones, and 1 : 8-dihydroxyanthraquinone (chrysazin), are deposited unchanged from thionyl chloride, even after their solutions have been boiled for periods of 48 to 60 hours. 2-Hydroxyanthraquinone also does not react with boiling thionyl chloride, and it would appear, therefore, that in anthrapurpurin the 7-hydroxyl group, which is converted into a chlorothionyl group, is rendered more reactive by the presence of other hydroxyl groups as substituents in the second benzene nucleus.

The work described here and in Part I (*loc. cit.*) indicates that two ortho-hydroxyl groups in the anthraquinone series will always react with thionyl chloride to give a thionyl derivative: 1 : 2-thionyl compounds react with carboxylic acids, giving 2-acyl derivatives only; this rule does not hold when the thionyl group is attached to the 2 : 3-position.

(I.) 

 (II.)

(III.) 

 (IV.)

Since the melting points given in the literature for several of the hydroxy-compounds and for their acetyl derivatives are low, new data have been tabulated at the end of this paper.

EXPERIMENTAL.

The hydroxyanthraquinones were obtained by the hydrolysis of their pure acetyl derivatives with concentrated sulphuric acid (see Part II, this vol., p. 1428). 5-*Chloro*-1-*hydroxyanthraquinone* was prepared from 5-amino-1-hydroxyanthraquinone by diazotisation. 1-Hydroxyanthraquinone and 2-hydroxyanthraquinone were

similarly obtained from the corresponding amines. All the acetyl derivatives were repeatedly crystallised from pyridine or pyridine–acetic anhydride.

The thionyl chloride was fractionated immediately before use.

Analyses.—On account of their instability, the thionyl compounds were analysed as soon as possible after preparation. Immediately before analysis the compounds were finely ground and heated for 20 minutes at 80—90° in order to remove traces of thionyl chloride and ether.

Thionylpurpurin (I).—Purpurin (10 g.) was boiled under reflux with 120 c.c. of thionyl chloride for 6 hours. The deep red solution was then concentrated to 50 c.c. and protected from moisture. Clusters of small, yellowish-brown crystals (8·5 g.) separated slowly; these were washed with absolute ether until free of thionyl chloride and stored in sealed tubes; m. p. 211—213° [Found : C, 55·3; H, 2·1; S, (*a*) by Carius's method, 10·6, and (*b*) iodometrically as sulphur dioxide produced by boiling with glacial acetic acid, 10·3; *M*, cryoscopic in naphthalene, 320, 325. $C_{14}H_6O_6S$ requires C, 55·6; H, 2·0; S, 10·6%; *M*, 302].

Thionylpurpurin is rapidly decomposed by moisture, and 0·7320 g., after standing in air for 24 hours followed by drying in a vacuum over sulphuric acid, yielded 0·6185 g. of purpurin (theory requires 0·6205 g.). This was recognised by conversion into the triacetate, by comparison with an authentic specimen (mixed melting point 256—258°), and by analysis (Found : C, 65·4; H, 3·2. Calc. : C, 65·6; H, 3·1%).

2-Acetylpurpurin was obtained by boiling 2·5 g. of thionylpurpurin with 50 c.c. of glacial acetic acid for 40 minutes. The cooled solution deposited 2·0 g. of orange-red crystals which, after recrystallisation from toluene, melted at 168—170° (Found : C, 64·5; H, 3·4; CH_3·CO, 14·0. Calc. : C, 64·4; H, 3·4; CH_3·CO, 14·4%).* The product was identical with that obtained by the monoacetylation of purpurin in pyridine.

1 : 2-*Thionyl*-7-*chlorothionylanthrapurpurin* (II).—Anthrapurpurin (10 g.) was boiled with thionyl chloride (200 c.c.) for 9 hours; the light red solution was concentrated to 30 c.c. and kept in the dry. The small, ochre-coloured crystals (14 g.) that separated were washed with dry benzene and absolute ether; they were very sparingly soluble in all common organic solvents and melted at 179° (decomp.) (Found : C, 43·9; H, 1·4; Cl, 9·3; S, 16·6. $C_{14}H_5O_7ClS_2$ requires C, 43·7; H, 1·3; Cl, 9·2; S, 16·6%). When 1·304 g. were kept in the air, decomposition occurred rapidly with

* When acetyl derivatives were sparingly soluble in alcohol, A. G. Perkin's device (J., 1925, **127**, 1886) of dissolving them in concentrated sulphuric acid before estimation by the ethyl acetate method, was adopted.

the evolution of fumes, and the product after drying was 0·924 g. of anthrapurpurin (theory requires 0·923 g.), which was recognised by a mixed melting-point determination and by analysis (Found : C, 65·6; H, 3·2. Calc. : C, 65·6; H, 3·1%).

2-*Acetylanthrapurpurin*, $C_{14}H_7O_5{\cdot}CO{\cdot}CH_3$.—The preceding compound (2 g.) was sifted into boiling glacial acetic acid (30 c.c.). Sulphur dioxide and hydrogen chloride were evolved, and yellow crystals (1·5 g.) of 2-*acetylanthrapurpurin* separated from the hot solution. These melted at 296—298° with charring, and this melting point was unchanged by further recrystallisation (Found : C, 64·2; H, 3·4; $CH_3{\cdot}CO$, 14·1. $C_{14}H_7O_5{\cdot}CO{\cdot}CH_3$ requires C, 64·4; H, 3·4; $CH_3{\cdot}CO$, 14·4%). When 0·70 g. of this product dissolved in hot pyridine was treated with 0·25 c.c. (2 mols.) of acetic anhydride, the red solution became pale yellow and on cooling deposited 0·79 g. of pure triacetylanthrapurpurin, which was identified by comparison with an authentic specimen.

2-*Benzoylanthrapurpurin*, $C_{14}H_7O_5{\cdot}CO{\cdot}C_6H_5$.—A mixture of 2·5 g. of the chlorothionyl compound and 2·0 g. of dry benzoic acid was heated at 170° until the evolution of gas ceased (about 10 minutes). The product was twice crystallised from tetrachloroethane, from which 2-*benzoylanthrapurpurin* separated in clusters of microscopic, yellow needles, m. p. 203—205° (Found : C, 70·2; H, 3·4. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3%). The compound is sparingly soluble in boiling acetic acid or benzene, more soluble in hot toluene, and very soluble in boiling tetrachloroethane.

Triacetylanthrapurpurin.—The chlorothionyl compound (2·0 g.) was added slowly to boiling acetic anhydride (10 c.c.). After 15 minutes, the pale red solution was cooled and deposited 1·5 g. of triacetylanthrapurpurin as yellow plates, melting at 225—227° alone or when mixed with a pure specimen (Found : $CH_3{\cdot}CO$, 33·1. Calc. : $CH_3{\cdot}CO$, 33·0%).

Thionylhystazarin (III).—After boiling for 12 hours with 400 c.c. of thionyl chloride, 7 g. of hystazarin had dissolved to a red solution, which was concentrated to 50 c.c. The pale yellowish-green, rectangular plates which separated (6·8 g.; and 0·8 g. on further concentration of the filtrate) were filtered off rapidly and washed with absolute ether; m. p. 200° (Found : C, 58·5; H, 2·1; S, 11·0; *M*, cryoscopic in naphthalene, 295. $C_{14}H_6O_5S$ requires C, 58·7; H, 2·1; S, 11·2%; *M*, 286). After standing in moist air for 3 weeks, 0·249 g. gave, when dried, 0·214 g. (0·209 g. theoretical) of hystazarin (Found : C, 69·8; H, 3·4. Calc. : C, 70·0; H, 3·3%).

Interaction with Acetic Acid.—Thionylhystazarin (1·5 g.) was dissolved in 100 c.c. of boiling acetic acid, and yellow crystals soon began to separate. After 45 minutes, the solution was cooled and the crystals (1·2 g.) were collected. These contained no sulphur,

and were identified as hystazarin by comparison and by analysis (Found : C, 70·0; H, 3·1. Calc. : C, 70·0; H, 3·3%). The yellow precipitate obtained by stirring the filtrate into water apparently consisted of pure hystazarin only (Found : C, 69·8; H, 3·3%).

Diacetylhystazarin.—A solution of the thionyl compound in acetic anhydride was boiled for 1 hour. The fine, pale yellow needles obtained melted at 211—213°, alone and when mixed with pure diacetylhystazarin (Found : C, 66·5; H, 3·7; CH_3·CO, 26·3. Calc. : C, 66·7; H, 3·7; CH_3·CO, 26·5%). When recrystallised from pyridine, the substance was obtained as pale greenish-yellow plates with the same melting point.

2 : 3-*Thionylanthragallol* (IV).—When 4 g. of anthragallol * had been treated with 80 c.c. of boiling thionyl chloride for 1½ hours, a dark green solution was suddenly formed. After 5 hours' further boiling, the evolution of hydrogen chloride had almost ceased and the solution was concentrated to about 30 c.c. After 12 hours, slender, greenish-yellow rods (3·0 g.) of 2 : 3-*thionylanthragallol* were filtered off, and washed thoroughly with absolute ether. The filtrate on concentration yielded a further 0·7 g. The product, which was free from chlorine, melted at 218—220°, with previous slight sintering (Found : C, 55·4; H, 2·0; S, 10·6; *M*, in freezing naphthalene, 290, 300. $C_{14}H_6O_6S$ requires C, 55·6; H, 2·0; S, 10·6%; *M*, 302). After 0·3796 g. of the thionyl compound had been exposed to the air for 10 days, it yielded, when dried, 0·3208 g. (0·3218 g. theoretical) of anthragallol, m. p. 312—314° (Found : C, 65·4; H, 3·2. Calc. : C, 65·6; H, 3·1%).

2 : 3-*Diacetylanthragallol.*—Finely-powdered thionylanthragallol (2 g.) was sifted into boiling acetic anhydride (60 c.c.). The yellowish-green solution was boiled for 10 minutes and then rapidly stirred into ice-water. The yellow precipitate (2·4 g.) was washed with cold water. It melted at 213—216° and, after two crystallisations from pure acetone, at 223—224°, either alone or when mixed with authentic 2 : 3-diacetylanthragallol prepared by the partial acetylation of anthragallol in pyridine solution (Found : C, 63·3; H, 3·5; CH_3·CO, 25·4. Calc. : C, 63·5; H, 3·5; CH_3·CO, 25·3%).

Interaction of 2 : 3-*Thionylanthragallol with Acetic Acid.*—(A) *Anthragallol.*—In a typical preparation thionylanthragallol (1·65 g.) was boiled for 45 minutes with glacial acetic acid (160 c.c.). The red solution, after 2 days, deposited 0·55 g. of anthragallol as light brown spherules, m. p. 313—314° (Found : C, 65·5; H, 3·1. Calc. : C, 65·6; H, 3·1%). After concentration to 30 c.c., the filtrate yielded a further 0·45 g., m. p. 312—314° (Found : C, 65·6; H,

* Anthragallol was obtained from Anthracene Brown, W. by extraction with nitrobenzene. I am indebted to Professor A. G. Perkin, F.R.S., for informing me of this method.

3·2%). Both melting points were unchanged when the specimens were mixed with pure anthragallol.

(B) 3-*Monoacetylanthragallol.*—When the filtrate from the second crop of anthragallol was stirred into cold water, 0·55 g. of a golden-brown solid, m. p. 206—209°, separated, which crystallised from toluene in small, golden-brown rods, m. p. 210—212° (Found: C, 64·5; H, 3·2; CH_3·CO, 14·0. $C_{14}H_7O_5$·CO·CH_3 requires C, 64·4; H, 3·4; CH_3·CO, 14·4%).

5-*Chloro*-1-*hydroxyanthraquinone.*—A solution of 5-chloro-1-amino-anthraquinone (10 g.) in concentrated sulphuric acid (100 c.c.) was treated at 0° with powdered sodium nitrite (3·0 g.) during 1 hour and then stirred for 8 hours. On the next day, the mixture was heated at 130—140° for 5 minutes and poured into 2 litres of cold water; the resulting suspension was boiled and filtered. The bright yellow solid obtained was dissolved in 2% aqueous caustic soda, and the solution was filtered (to remove unchanged amine) into boiling hydrochloric acid. The golden-yellow product melted at 221—222°.

5-*Chloro*-1-*acetoxyanthraquinone.*—The hydroxy-compound was boiled with a mixture of acetic anhydride and pyridine. The *acetyl* compound formed crystallised from a similar mixture in pale primrose needles, m. p. 205° (Found: Cl, 11·6; CH_3·CO, 14·3. $C_{14}H_6O_3Cl$·CO·CH_3 requires Cl, 11·8; CH_3·CO, 14·3%). When hydrolysed by boiling with a solution of sulphuric acid in absolute alcohol, it gave 5-*chloro*-1-*hydroxyanthraquinone* in bright golden-yellow, rectangular plates, m. p. 223—224° (Found: C, 65·1; H, 2·8; Cl, 13·6. $C_{14}H_7O_3Cl$ requires C, 65·0; H, 2·7; Cl, 13·7%).

The melting points given below were determined with short-stemmed thermometers.

Hydroxy-compounds (crystallised from alcohol).	M. p.	Completely acetylated derivatives (crystallised from pyridine).	M. p.
1-Hydroxyanthraquinone, pale primrose needles.	191—192°	Small, pale primrose plates.	183—185°
2-Hydroxyanthraquinone, pale yellow needles.	305	Fine, stone-coloured needles.	160
4-Chloro-1-hydroxy-anthraquinone, golden-yellow needles.	193—194	Pale primrose needles.	176—177
Hystazarin.	—	Pale greenish-yellow plates.	211—213
Chrysazin, small, golden-yellow plates.	Orange-red at 160°, m. p. 193°.	Hexagonal, yellow plates.	244—245
Anthragallol, fine, orange-brown needles.	313—314	Very fine, yellow rods.	188—189
Purpurin, very fine, deep red needles.	257—259	Short, yellow rods.	203—205
Anthrapurpurin.	—	Pale yellow plates.	226—228

The author wishes to express his indebtedness to the Research Fund Committee of the Chemical Society, by whom a portion of the expenses of this research has been defrayed, and also to the following manufacturers for gifts of materials: The British Alizarine Company, Limited; I.G. Farbenindustrie Aktiengesellschaft, Leverkusen; and The Scottish Dyes, Limited.

THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, May 17th,* 1926.]