## 174. *Halogenation in the Anthraquinone Series.*

By Frank H. Day.

The sulpho-groups in anthraquinonesulphonic acids in aqueous solution can be replaced by bromine at high temperatures, giving bromoanthraquinones. α-Carboxyl groups can be replaced by chlorine or bromine under similar conditions. There is some evidence that nitro-groups can be replaced by chlorine by the action of hydrochloric acid at high temperatures.

The action of chlorine and bromine on aqueous solutions of hydroxyanthraquinonesulphonic acids at 100° leads to disruptive oxidation, but at the ordinary temperature several of the sulphonic acids react with bromine, yielding bromohydroxyanthraquinonesulphonic acids. The sulpho-group of 1-aminoanthraquinone-2-sulphonic acid, however, is also replaced, giving dibromoaminoanthraquinone.

The preparation of chloroanthraquinones from dilute aqueous solutions of anthraquinonesulphonic acids by heating with a chlorate and hydrochloric acid at 100° is well known (Ullmann, *Annalen*, 1911, **381**, 2; Schilling, *Ber.*, 1913, **46**, 1066; Goldberg J., 1931, 1771). Patent claims that bromoanthraquinones can be prepared in a similar manner cannot be substantiated: a reaction mixture behaving in a strictly analogous manner to the chlorate and hydrochloric acid cannot be reproduced with bromine compounds.

The possibility of replacing α-sulpho-groups by means of molecular bromine depends on the use of a high temperature: in sealed tubes at 250°, satisfactory yields of 1-bromoanthraquinone were obtained from anthraquinone-1-sulphonic acid. There is evidence that 1 : 5- and 1 : 8-dibromoanthraquinones are formed in a similar manner but in very small yield. So far it has not been found possible to replace β-sulpho-groups in this way and no evidence was obtained of any action at temperatures up to 260°. An attempt was made to extend the method to iodination and some evidence of the formation of minute yields of iodoanthraquinone was obtained.

Anthraquinone-1-carboxylic acid in aqueous suspension is converted into 1-chloroanthraquinone by heating with a chlorate and hydrochloric acid at 200° and into 1-bromoanthraquinone by molecular bromine at 200°. Experiments on the β-carboxylic acid have so far given negative results.

Claims (D.R.-Pp. 128845, 252578, 254450) that treatment of nitroanthraquinones in inert solvents with chlorine at 160° leads to replacement of the nitro-group have not been substantiated. In attempts to replace the nitro-group in 1-nitroanthraquinone by chlorine by heating with hydrochloric acid at 280—300° (cf. *Ber.*, 1896, **29**, 594) a product was obtained which appears to be a very impure chloroanthraquinone.

In contrast to the behaviour of the simple negatively substituted anthraquinones the sulphonic acids of hydroxy- and amino-anthraquinones are remarkably reactive towards halogens, but the reactivity is due entirely to the hydroxy- and amino-groups, the sulpho-groups in general not being affected: several bromohydroxyanthraquinonesulphonic acids and a dibromoaminoanthraquinone have thus been prepared. The sulphonic acids used were all β-sulphonic acids, the α-sulphonic acids being difficult of access. The substances studied were 1-hydroxyanthraquinone-2-sulphonic acid, anthrarufin-2 : 6-disulphonic acid, alizarin-3-sulphonic acid, quinizarin-3-sulphonic acid, and 1-aminoanthraquinone-2-sulphonic acid. In the first instance the acids were submitted to chlorination under conditions similar to those usually employed for preparing the simple chloroanthraquinones, *viz.*, moderately dilute aqueous solutions were treated at 100° with a chlorate and hydrochloric acid. This treatment leads to disruption of the anthraquinone ring system by oxidation, giving in every case colourless non-anthraquinonoid substances. In experiments with nascent and molecular bromine under the same conditions disruptive oxidation of all the hydroxyanthraquinonesulphonic acids occurred as above. 1-Aminoanthraquinone-2-sulphonic acid is, however, more stable and when treated with molecular bromine at 100° or even in the cold it readily yields 2 : 4-dibromo-1-aminoanthraquinone.

Treatment of the hydroxyanthraquinonesulphonic acids in cold aqueous solution with molecular bromine led to the formation of sparingly soluble bromohydroxyanthraquinonesulphonic acids, which usually separated. From quinizarin-3-sulphonic acid, however, no bromo-derivative was obtained; here the *p*-position to a hydroxyl group, which is usually the point of entry of bromine, is occupied. The presence of hydroxy-groups in each nucleus of anthrarufin-2 : 6-disulphonic acid enhances reactivity to such an extent that with excess of bromine a tetrabromo-derivative is readily obtained (D.R.-P. 197,082 claims the formation of a dibromo-derivative under similar conditions). The action of bromine on an aqueous solution of alizarin saphirol (4 : 8-diaminoanthrarufin-2 : 6-disulphonic acid) leads to the formation of a deep magenta-coloured solution possessing dyeing properties, but the substance has not been isolated in a pure form.

The chief interest of these reactions lies in the facts that they show the dominant effect of hydroxy- and amino-groups as activating influences in the anthraquinone molecule and that replacement of sulpho-groups by halogen is not possible when those groups are present, except in the case of 1-aminoanthraquinone-2-sulphonic acid; here the sulpho-group is replaced with great ease, whereas, as previously indicated, this operation can only be carried out with the simple sulphonic acids with considerable difficulty.

## Experimental.

*Action of Bromine on Anthraquinone-1-sulphonic Acid.*—A mixture of potassium anthraquinone-1-sulphonate (2 g.) in water (20 c.c.), 25% hydrobromic acid (4 g.), and bromine (2 g.) was heated in a sealed tube at 250° for 24 hours. The solid product was an orange cake of 1-bromoanthraquinone. It was boiled with water to remove soluble salts and crystallised from acetic acid; yield 1·05 g., m. p. 188° (Found: Br, 28·0. Calc.: Br, 27·9%).

*Bromination of the α-Disulphonates.*—Similar treatment of the 1 : 5- and the 1 : 8-disulphonate gave minute quantities of brown and dark red crystalline products respectively. These gave qualitative reactions for bromine. No intermediate monobromo-sulphonic acid could be detected in either case.

*Action of Iodine on the 1-Sulphonic Acid.*—25 C.c. of a saturated aqueous solution of the 1-sulphonic acid were heated with 1 g. of iodine at 250° for 12 hours. The residue after removal of soluble matter consisted of dark yellow crystals (0·05 g.) and gave a qualitative reaction for iodine.

*Action of Chlorine on Anthraquinone-1-carboxylic Acid.*—The acid (1 g.) was heated with dilute hydrochloric acid (20 c.c.) and sodium chlorate (1 g.) in a sealed tube at 200° for 12 hours; carbon dioxide was produced. The product, after being boiled with dilute sodium hydroxide solution to remove unchanged carboxylic acid, separated from acetic acid in pale yellow crystals (0·5 g.), m. p. 155° (Found: Cl, 14·6. Calc.: Cl, 14·7%).

*Action of Bromine on the 1-Carboxylic Acid.*—The acid (1 g.) was heated as above with water (20 c.c.) and bromine (1 g.) for 12 hours at 200°. The product, similarly treated, consisted of pale yellow crystals (0·5 g.), m. p. 185° (Found: Br, 27·2. Calc.: Br, 27·9%).

*Action of Hydrochloric Acid on 1-Nitroanthraquinone.*—The substance (1 g.) was heated with concentrated hydrochloric acid (20 c.c.) in a sealed tube at 250° for 6 hours and then at 280° for 6 hours. The brownish cake obtained, after crystallisation from acetic acid, had m. p. 133—135°, depressed by 1-chloroanthraquinone, but raised by 2-chloroanthraquinone (Found: Cl, 14·5. Calc.: Cl, 14·7%). The substance was not reduced by sodium sulphide and contained no nitrogen.

*4-Bromo-1-hydroxyanthraquinone-2-sulphonic Acid.*—1-Hydroxyanthraquinone (20 g.) was heated at 120° with 20% fuming sulphuric acid (100 g.) until a drop of the melt was completely soluble in water. The mixture was run into cold water (1 l.) and filtered and an excess (30 g.) of bromine, dissolved in potassium bromide solution, was added during 2 hours. The yellowish-orange solid which separated (21 g.) was crystallised from hot water (Found: Br, 20·0; S, 8·4. $C_{14}H_7O_6BrS$ requires Br, 20·8; S, 8·3%). The *sulphonic acid* was soluble in hot water and sparingly in cold. From hot solutions, potassium chloride precipitated the potassium salt. The position of the bromine atom was proved (*a*) by heating the potassium salt with baryta and water at 200°, a minute yield of purpurin (1 : 2 : 4-trihydroxyanthraquinone) being obtained, recognised by m. p. and by formation of a fluorescent solution with boiling alum, and (*b*) by heating with 80% sulphuric acid at 170° for a few minutes, 4-bromo-1-hydroxyanthraquinone, m. p. 184°, being formed.

*Tetrabromoanthrarufin-2 : 6-disulphonic Acid.*—This was prepared by a similar method to that used for the previous substance or (as the potassium salt) as follows: A saturated aqueous solution of potassium anthrarufin-2 : 6-disulphonate (2 l.) was treated with an excess of bromine in the cold. After some hours separation of the bromo-compound was complete. The sparingly soluble *potassium* salt was collected, boiled with water to remove any unchanged anthrarufin-disulphonate, and obtained as an orange-red solid (Found: Br, 42·0; S, 8·0. $C_{14}H_2O_{10}Br_4S_2K_2$ requires Br, 41·4; S, 8·3%). Its solubility in water at 100° was less than 1 part in 4000. When warmed with aqueous ammonia and a trace of copper, it gave a dark blue solution, probably of an amino-hydroxy-sulphonic acid, which dyed wool blue. 4-Bromo-1-hydroxyanthraquinone-2-sulphonic acid does not react in this way.

*Potassium 4-Bromoalizarin-3-sulphonate.*—200 C.c. of a 1% solution of alizarin-3-sulphonic acid were treated with an excess (4 g.) of bromine and kept for several hours. On addition of potassium chloride (20 g.) the *potassium* salt of the brominated acid separated; it crystallised from hot water as a red solid (Found: Br, 16·8; K, 10·1; loss at 120°, 8·9. $C_{14}H_6O_7BrSK,2H_2O$ requires Br, 16·9; K, 9·95; $H_2O$, 9·2%). The bromine atom is regarded as having entered the substituted nucleus at the only available position, *viz.*, 4.

*Bromination of 1-Aminoanthraquinone-2-sulphonic Acid.*—This may be carried out at the ordinary temperature, but better results are obtained at 100°. 500 C.c. of a 1% solution of sodium 1-aminoanthraquinone-2-sulphonate were acidified with hydrobromic acid and boiled under reflux while 5 g. of bromine, dissolved in potassium bromide solution, were gradually run in. There was immediate separation of a scarlet precipitate and no bromine fumes were observed in the condenser. After 3 hours the product was collected (4·7 g.) and crystallised from acetic acid. The scarlet powder obtained had m. p. 214° and left no residue on ignition (Found: Br, 41·2. Calc. for $C_{14}H_7O_2NBr_2$: Br, 42·0%). The usual influence of the amino-group in halogenation being taken into account, it is probable that one bromine atom enters at position 4, and the other bromine atom presumably replaces the sulpho-group at position 2. The substance is therefore identified with 2 : 4-dibromo-1-aminoanthraquinone, with which it agrees in appearance and properties.

The author's thanks are due to Imperial Chemical Industries Ltd. for gift of materials.

CARLISLE TECHNICAL COLLEGE. [*Received, March 2nd,* 1939.]