

## 10. *The Reduction of Heteronuclear Nitroanthraquinonesulphonates.*

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NITROANTHRAQUINONES have frequently been reduced to aminoanthraquinones, but little is known of the intermediate compounds.

Hydroxylaminoanthraquinones have been isolated (Schmidt and Gattermann, *Ber.*, 1896, **29**, 2934; Wacker, *Ber.*, 1902, **35**, 666; D.R.-P. 67,102, 96,197), and less highly hydrogenated intermediates obtained from them by mild oxidation (Wacker, *loc. cit.*; Beisler and Jones, *J. Amer. Chem. Soc.*, 1922, **44**, 2296; D.R.-P. 363,930, 411,531). Scholle and Eberle (*Monatsh.*, 1911, **32**, 1035), however, obtained 2-azoxyanthraquinone by direct reduction of 2-nitroanthraquinone with glucose.

For the reduction of nitroanthraquinones to the corresponding

aminoanthraquinones, boiling aqueous sodium sulphide is regarded as the best reagent (Barnett, "Anthracene and Anthraquinone," p. 192), but intermediate compounds have not previously been isolated by its use.

The action of aqueous sodium sulphide at or below 0° on sodium 1-nitroanthraquinone-5- and -8-sulphonates has been found to give *sodium 1-hydroxylaminoanthraquinone-5- and -8-sulphonates* in almost theoretical yields, there being little or no tendency for further reduction. By diminishing the ratio of sodium sulphide to the nitro-sulphonate, less highly hydrogenated substances are formed which, since they do not give the nitroso-reaction, are considered to be *sodium 1-azoxyanthraquinone-5- and -8-sulphonates*.

Treatment of the hydroxylamino-sulphonates with hot sulphuric acid causes migration of the *N*-hydroxyl to the nucleus, giving *sodium 1-amino-4-hydroxyanthraquinone-5- and -8-sulphonates*.

The method described for the production of derivatives of anthraquinone is more convenient and more easily controlled than those involving the use of stannite, glucose, etc.

#### EXPERIMENTAL.

*Sodium 1-Nitroanthraquinone-5- and -8-sulphonates*.—Sodium anthraquinone-1-sulphonate was nitrated by the method of Ullmann and Kertész (*Ber.*, 1919, **52**, 525). The 1:5-isomeride, which separated from the warm sulphuric acid, was collected on asbestos, dissolved in water, precipitated by saturated sodium chloride solution, and recrystallised. The 1:8-isomeride in the sulphuric acid filtrate was isolated (E.P. 17,565/1903), and recrystallised, small head fractions being rejected each time, until the chloro-nitroanthraquinone derived from a sample by chlorination had the correct melting point.

*Sodium 1-Azoxanthraquinone-5-sulphonate*.—To a paste of sodium 1-nitroanthraquinone-5-sulphonate (20 g.) and water (40 c.c.), a solution of crystalline sodium sulphide (8 g.) in water (40 c.c.) was added, and the mixture stirred for 15 minutes, the temperature being -4° throughout. Addition of hydrochloric acid (40 c.c.) produced a semi-solid mass, which was drained, washed with a little cold water, and crystallised twice from boiling water, *sodium 1-azoxanthraquinone-5-sulphonate* (12 g.) being obtained in reddish-brown leaves (Found in dehydrated salt: S, 9.8.  $C_{28}H_{12}O_{11}N_2S_2Na_2$  requires S, 9.7%). The salt dissolves with difficulty in boiling water, giving a stable, pale reddish-brown solution, unchanged by acid or alkali; the alkaline solution becomes deep green on addition of aqueous sodium sulphide owing to reduction to the hydroxyl-amino-sulphonate.

*Sodium 1-Hydroxylaminoanthraquinone-5-sulphonate.*—Sodium 1-nitroanthraquinone-5-sulphonate was reduced (at  $-2^{\circ}$ ; 25 mins.) as in the preceding experiment (crystalline sodium sulphide, 20 g. instead of 8 g.). The product of the acidification with hydrochloric acid (1:1; 50 c.c.), treated as described above, a small head fraction being rejected at each crystallisation, gave *sodium 1-hydroxylaminoanthraquinone-5-sulphonate* in dark red needles with a metallic iridescence (Found in dehydrated salt: S, 9.6.  $C_{14}H_8O_6NSNa$  requires S, 9.4%). The salt is much more easily soluble in boiling water than the corresponding azoxy-compound, giving a deep purple-red solution which slowly decomposes. The colour of the solution is unchanged on acidification, but the addition of alkali produces an intense deep green colour, doubtless due to the formation of the disodium salt. The colour change is sharp and takes place between  $p_H$  9 and 10.5 as determined by comparison with B.D.H. universal indicator.

*Sodium 1-Amino-4-hydroxyanthraquinone-5-sulphonate.*—A solution of sodium 1-hydroxylaminoanthraquinone-5-sulphonate (15 g.) in sulphuric acid (60 c.c.) was heated on the steam-bath until a test portion gave a violet (instead of blue) coloration on dilution and basification with caustic alkali ( $1\frac{1}{4}$ — $1\frac{1}{2}$  hours). The cooled product was poured on ice (200 g.) and the precipitate (12 g.) was collected, dissolved in dilute aqueous sodium hydroxide, and reprecipitated from the filtered, cooled, violet solution by the addition of dilute sulphuric acid. The sulphate of 1-amino-4-hydroxyanthraquinone-5-sulphonate was thus obtained as an amorphous curry-coloured powder, difficultly soluble in water, giving a solution with a carmine colour due to hydrolysis.

The sulphate was suspended in a small quantity of water and treated with aqueous sodium hydroxide until it just dissolved. When the purple-red solution was concentrated, *sodium 1-amino-4-hydroxyanthraquinone-5-sulphonate* separated in dark red needles, which were recrystallised (Found in dehydrated salt: S, 9.7; Na, 6.5.  $C_{14}H_8O_6NSNa$  requires S, 9.4; Na, 6.75%). It is easily soluble in boiling water, giving a violet-red solution, which becomes deep purple on addition of alkali; the colour change is fairly sharp. The alkaline solution dyes silk a fine purple shade.

Reduction of the above azoxy-sulphonate and hydroxylamino-sulphonate with boiling aqueous sodium sulphide gave sodium 1-aminoanthraquinone-5-sulphonate. Acidification of the concentrated aqueous solution of the sodium salt precipitated the free acid, which crystallised from water in reddish-brown spangles (Found: S, 10.7. Calc. for  $C_{14}H_9O_5NS$ : S, 10.6%).

*Derivatives of Sodium 1-Nitroanthraquinone-8-sulphonate.*—By

the methods described above, the following compounds were obtained from this salt : *sodium 1-azoxyanthraquinone-8-sulphonate* (Found in dehydrated salt : S, 9.9%), *sodium 1-hydroxylaminoanthraquinone-8-sulphonate* (Found in dehydrated salt : S, 9.8%), and *sodium 1-amino-4-hydroxyanthraquinone-8-sulphonate* (Found in dehydrated salt : Na, 6.6%). These substances have properties and crystalline forms almost identical with those of the isomeric 5-sulphonates, but are rather more soluble.

None of the compounds mentioned above has any action on *T. equiperdum* in mice.

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