47. *Hydroxyanthraquinones. Part II.* 1 : 2 : 5 : 6- *and* 1 : 4 : 5 : 8-*Tetrahydroxyanthraquinones.*

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Following the work reported in Part I (J., 1931, 3206), it was considered of interest to investigate the sulphonation of anthrarufin and the production of the corresponding hydroxyanthraquinone obtained by alkali fusion of the sodium salt.

Whilst quinizarin gives a quantitative yield of the sodium 2-sulphonate on boiling with aqueous sodium sulphite in the presence of copper oxide (*loc. cit.*), alizarin does not react when similarly treated and only an infinitesimal amount of a water-soluble product (? sulphonate) is formed from anthrarufin even after boiling for 24 hours under the above conditions. Anthrarufin has been reported to yield the disulphonic acid on heating with 4 parts of 20% oleum at 100—120° until completely soluble in water (Baeyer & Co., *Zentr.*, 1898, I, 1255), but no further details are given. In the present work the disulphonic acid was produced in good yield by a brief heating at 140—150° with 3—4 parts of 20% oleum. It has also been reported (Baeyer & Co., D.R.P. 103,988) that the sodium salt of the sulphonic acid yields, on alkali fusion at 200—280°, 1 : 2 : 5 : 6-tetrahydroxyanthraquinone; no further details of the conditions or yield are given. The author found that the reaction does not proceed to any appreciable extent at 200—230°, and at 280° decomposition is so extensive that very little of the desired product can be isolated. It is possible, however, to obtain a yield of 70—75% by proper control of the conditions. The 1 : 2 : 5 : 6-tetrahydroxyanthraquinone obtained can be sulphonated by heating with 3—4 parts of 20% oleum at 120—130°; a yield of over 90% of the sodium salt of the disulphonic acid is obtained. Repeated attempts to produce the corresponding hexahydroxyanthraquinone by alkali fusion under various conditions, with or without the addition of sodium chlorate, were unsuccessful.

It seemed more likely that 1 : 4 : 5 : 8-*tetrahydroxyanthraquinone* would behave similarly to quinizarin on boiling with sodium sulphite in the presence of copper oxide. The preparation of this substance was therefore undertaken. It was not found possible to obtain it by diazotisation of diaminoanthrarufin in concentrated sulphuric acid solution, followed by dilution and boiling in the usual way; the chocolate-brown product was almost insoluble in concentrated sulphuric acid, aqueous sodium hydroxide or nitrobenzene. The leuco-compound of 1 : 4 : 5 : 8-tetrahydroxyanthraquinone was, however, obtained in good yield by boiling diaminoanthrarufin in alkaline solution with sodium hyposulphite, and this can be quantitatively oxidised by a brief boiling in nitrobenzene solution, from which the anthraquinone derivative crystallises on cooling. It cannot be sulphonated by boiling with aqueous sodium sulphite in the presence of copper oxide.

Experimental.

Anthrarufindisulphonic Acid.—50 G. of anthrarufin and 90 c.c. of 20% oleum were heated at 120° for 3 hours. The cooled melt was poured into 2½ l. of water, the filtered, dark orange-brown solution warmed to 60°, and the sodium salt of the disulphonic acid precipitated by addition of sodium chloride. The product was dissolved in 5 l. of hot water, 50 g. of sodium chloride added, and the sodium salt allowed to crystallise. Yield, 70 g.

1 : 2 : 5 : 6-*Tetrahydroxyanthraquinone.*—40 G. of sodium hydroxide were heated in a nickel crucible with a little water and 1 g. of sodium chlorate until molten, and 10 g. of disodium anthrarufindisulphonate were gradually stirred in. The temperature was then raised to 260—270° for 15 minutes with continuous stirring. After cooling, the mass was extracted with 1 l. of hot water and acidified with hydrochloric acid. The orange-brown precipitate was collected, washed with a large volume of hot water, and dried. Yield, 4·6 g. (75%). The product crystallises in pure condition from pyridine in orange-red needles, m. p. > 300° (Found: C, 62·3; H, 3·0. Calc. for $C_{14}H_8O_6$: C, 61·8; H, 2·9%); it dissolves in alkalis with a crimson, and in concentrated sulphuric acid with a purple colour. The *tetra-acetyl* derivative occurs in yellow needles, m. p. 260—275° (decomp.) (Found: C, 59·2; H, 3·6. $C_{22}H_{16}O_{10}$ requires C, 60·0; H, 3·6%).

Leuco-1 : 4 : 5 : 8-*tetrahydroxyanthraquinone.*—A mixture of 40 g. of diaminoanthrarufin, 80 g. of sodium hydroxide, and 2 l. of water was heated to boiling, 80 g. of sodium hyposulphite

added gradually, and boiling continued for 1 hour until ammonia was no longer evolved, the final volume being 1000—1500 c.c. When cold, the sodium salt of the leuco-compound was filtered off, washed with water, and dried (dark needles with bronze-green reflex). Yield, 48 g. (80%). The free leuco-compound was obtained in theoretical yield by suspending the sodium salt in hot water and acidifying with hydrochloric acid. It crystallised from glacial acetic acid in bronze needles, m. p. > 290° (decomp.) (acetyl derivative m. p. 235—240° decomp.).

1 : 4 : 5 : 8-*Tetrahydroxyanthraquinone* was obtained by heating 32 g. of the leuco-compound with 250 c.c. of nitrobenzene almost to boiling; the orange-brown solution rapidly became crimson, and the heat of the reaction caused the mixture to boil gently for a few minutes. Water was evolved and the solution was boiled for a brief period to expel it. After 12 hours the solution became blue-violet, probably owing to traces of unchanged diaminoanthrarufin. The *product*, which occurred as dark brown to black shining needles, was filtered off and washed with nitrobenzene and a large volume of ether. The yield was almost theoretical; m. p. > 300° (Found : C, 61·5; H, 3·0. $C_{14}H_8O_6$ requires C, 61·8; H, 2·9%). The product dissolved in glacial acetic acid with a crimson colour (cf. diaminoanthrarufin, which yields a blue solution). The *acetyl* derivative, prepared in the usual way, crystallised from glacial acetic acid in brownish-yellow needles, m. p. > 258° (decomp.) (Found : C, 60·1; H, 3·5. $C_{22}H_{16}O_{10}$ requires C, 60·0; H, 3·6%).

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