II.—*The Nitration of Benzeneazosalicylic Acid.*

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ALTHOUGH nitro-derivatives of benzeneazosalicylic acid have already been described, the compounds have been produced by coupling a diazotised nitraniline with salicylic acid, and hence contained the nitro-group in the benzene nucleus. By this process, Meldola (*Trans.*, 1885, 47, 666) obtained *p*-nitrobenzeneazosalicylic acid, and Gebek the corresponding meta-derivative (*Annalen*, 1888, 251, 188). Isomeric compounds containing a nitro-group in the salicylic acid residue have not hitherto been described, although from the results obtained on submitting benzeneazophenol to the action of warm dilute nitric acid (*Trans.*, 1900, 77, 99) it appeared very probable that a benzeneazo-*o*-nitrosalicylic acid should be formed by a similar nitration of benzeneazosalicylic acid. As a matter of fact, benzeneazosalicylic acid furnishes

a nitro-derivative different from any of the nitrobenzeneazosalicylic acids, and the compound produced was found to be identical with a synthetical benzeneazonitrosalicylic acid, in which the nitro-group stood in the ortho-position relatively to the hydroxyl group. On the other hand, benzeneazosalicylic acid nitrated in concentrated sulphuric acid solution furnished *p*-nitrobenzeneazosalicylic acid, the reaction therefore being quite analogous to that observed by Noelting (*Ber.*, 1887, 20, 2997) in the case of benzeneazophenol. This observation furnishes an indirect proof that even the azosalicylic acids are converted into quinonehydrazones by strong acids, although no salts with such acids have been isolated.

Ten grams of benzeneazosalicylic acid were made into a paste with 45 c.c. of water and 20 c.c. of nitric acid (sp. gr. 1.36), and warmed gently to 65–70°. The thermometer suddenly rose to about 85°, nitrous fumes were evolved, and a reddish, pasty mass resulted. This was quickly poured into water, cooled, and the flocculent precipitate collected and washed free from nitric acid with cold water. The substance, after drying, was usually found to weigh 5½ to 6 grams, and to melt between 160° and 170°. After two recrystallisations from dilute alcohol, a substance melting constantly at 197°* was obtained.

The substance separates in clusters of small, yellowish-red needles; it is easily soluble in alcohol, acetone, or glacial acetic acid, whilst it is also fairly easily soluble in boiling water. The solubility in hydrocarbon solvents is, however, slight. On analysis, results were obtained showing that the substance, crystallised from dilute alcohol and air dried, contains one molecular proportion of water of crystallisation.

0.8456 lost 0.0498 on drying at 110°. $H_2O = 5.88$.

0.1100 gave 13.2 c.c. moist nitrogen at 19° and 756 mm. $N = 13.72$.

$C_{13}H_9O_5N_3 \cdot H_2O$ requires $H_2O = 5.90$; $N = 13.80$ per cent.

The dried substance was also analysed :

0.0807 gave 0.1619 CO_2 and 0.0225 H_2O . $C = 54.72$; $H = 3.12$.

0.1112 „ 15.5 c.c. moist nitrogen at 23° and 746 mm. $N = 15.31$.

$C_{13}H_9O_5N_3$ requires $C = 54.32$; $H = 3.16$; $N = 14.66$ per cent.

In order to determine the constitution of the substance, various unsuccessful attempts were made to remove the carboxyl group. It was thought that prolonged heating with acetic anhydride might effect the

* This melting point as well as the others given in this paper are not corrected for the apparent coefficient of expansion of mercury.

elimination of carbon dioxide, whilst the hydroxyl group would be acetylated at the same time. Instead of this, the carboxyl group was found to be very firmly attached, and this and the nitro-group being both in ortho-positions relatively to the hydroxyl, protected the latter from acetylation. Heating in a reflux apparatus with benzoyl chloride led to the production of tarry substances, from which no crystalline matter could be isolated. The process of heating the barium salt with an excess of caustic baryta was also a failure, explosion regularly occurring as soon as a temperature of 155° was reached.

The substance had of necessity to be compared with a synthetical product obtained by coupling phenyldiazonium chloride with an alkaline solution of nitrosalicylic acid, $[\text{CO}_2\text{H} : \text{OH} : \text{NO}_2 = 1 : 2 : 3]$. The latter compound was obtained by nitration of salicylic acid in an acetic acid solution, and separated from the 1:2:5-isomeride by Hübner's method (*Annalen*, 1879, 195, 6), which depends on the sparing solubility of the barium salt of the 1:2:3-compound. The purity of the nitrosalicylic acid was checked by the melting point.

In coupling the nitrosalicylic acid with diazonium compounds, the same difficulty is experienced as in the case of *o*-nitrophenol, reaction taking place slowly and incompletely. Since the diazonium salt yields decomposition products difficult of removal, it is as well to use the nitrosalicylic acid in slight excess. The process consists in adding a well-cooled solution of phenyldiazonium chloride to an alkaline solution of nitrosalicylic acid, and allowing the interaction to proceed for three days in a cool place; the solution is then filtered from deposited matter and acidified. The precipitate contains the desired azo-compound mixed with a considerable excess of nitrosalicylic acid. To effect a separation, the mixed acids are dissolved in hot dilute ammonia solution and ammonium and barium chlorides added. Barium *o*-nitrosalicylate, although easily soluble in boiling water, is very sparingly-soluble in the cold, whilst the barium salt of the azo-acid dissolves very slightly even in boiling water. The precipitate obtained consists essentially, therefore, of barium benzeneazo-*o*-nitrosalicylate, and if the acid is liberated from the salt and the process of purification by means of the barium salts repeated, it is obtained in such a condition that when mixed with the product of direct nitration no depression of melting point is observed.

In addition to this direct proof of the constitution of the azo-acid, it may be mentioned that by reduction of an alkaline solution with hydrogen sulphide, aniline as one of the fission products may be detected with the greatest certainty by the ordinary reactions (volatility with steam, isonitrile reaction, bleaching powder test, and production of tribromoaniline). We have been unable to isolate the

diaminosalicic acid, which must form the other fission product, on account of its ready oxidisability.

Benzeneazo-*o*-nitrosalicic acid dissolves in concentrated sulphuric acid with a far yellower shade than benzeneazosalicic acid; possibly the nitro- and carboxyl groups in the ortho-position relatively to the hydroxyl exert a sufficient attraction on the hydrogen of the hydroxyl to prevent isomerisation of the compound to the quinone-hydrazone form. This subject will, it is hoped, be further examined; if it were found that nitration in concentrated sulphuric acid solution led to the production of *p*-nitrobenzeneazo-*o*-nitrosalicic acid, it would at least be rendered probable that isomerisation had taken place.

A solution of the acid in ammonia or fixed alkalis is red in colour. The ammonium salt was found to furnish the following precipitates:

Silver Nitrate.—Concentrated solutions give an orange precipitate somewhat soluble in water and easily soluble in ammonia.

Lead Acetate.—Yellowish-red precipitate insoluble in hot water.

Mercuric Chloride.—A yellow precipitate, somewhat soluble in a large quantity of water.

Stannous Chloride.—A yellow precipitate even in dilute solutions. This dissolves on warming, and does not appear to come down again on cooling. Excess of sodium hydroxide gives a deep red solution turned to a light red shade by excess of dilute hydrochloric acid.

Ferrous Sulphate.—A chocolate-coloured precipitate, turning greenish-brown on warming. The liquid becomes at the same time deep red.

Ferric Chloride.—A dark red solution and precipitate.

Cobalt Nitrate.—A yellow precipitate soluble in hot water.

Nickel Sulphate.—A dirty yellow precipitate soluble in hot water.

Magnesium Chloride.—An orange precipitate slightly soluble in hot water.

Barium and Calcium Chlorides.—Orange precipitates, soluble in a large quantity of boiling water.

Dyeing experiments were also made. Wool mordanted with iron gives a rich brown, with alumina a bright yellow, and with potassium dichromate, a dull yellow shade.

The *methyl ester* was prepared from 2 grams of the acid, 10–12 grams of methyl alcohol, and 1 c.c. of sulphuric acid. The mixture was warmed in a reflux apparatus for 5 hours, poured into water after the greater portion of the alcohol had been distilled off, and the precipitate collected, washed, and recrystallised from spirit. The substance forms small, brown needles melting at 132–134°.

0.0827 gave 0.1675 CO₂ and 0.0294 H₂O. C = 55.23 ; H = 3.95.

0.1080 „ 12.6 c.c. moist nitrogen at 18° and 760 mm. N = 13.48.

0.1094 „ 13.2 c.c. „ „ 18° „ 759 mm. N = 13.92.

C₁₄H₁₁O₅N₃ requires C = 55.77 ; H = 3.68 ; N = 13.96 per cent.

The *ethyl ester* was prepared in a similar manner from the acid, sulphuric acid, and 95 per cent. ethyl alcohol. It forms very small, yellow needles melting at 128—129°.

0.1290 gave 14.7 c.c. moist nitrogen at 22° and 760 mm. N = 12.91.

C₁₅H₁₃O₅N₃ requires N = 13.33 per cent.

p-Nitrobenzeneazosalicylic acid has already been described by Meldola (Trans., 1885, 47, 666). It may be obtained by gradually adding 2.1 grams of powdered potassium nitrate, in small portions at a time, to a solution of 5 grams of benzeneazosalicylic acid in 100 c.c. of concentrated sulphuric acid. Care should be taken that the temperature does not rise above 20° during the operation ; the mixture is then allowed to stand in the cold for 48 hours, after which it is poured into a large volume of water, collected, washed free from acid, and dried. The substance is already practically pure and the yield nearly theoretical. On recrystallisation, it was obtained as brilliant red needles. Meldola states that the melting point of the substance cannot be observed on account of blackening taking place above 225°. Our specimen, as well as one obtained from diazotised *p*-nitraniline and salicylic acid, did not blacken until a considerably higher temperature was reached, and by immersing the melting point tubes in sulphuric acid previously heated to 245—250°, both specimens were observed to melt at 253—254° (uncorr.), decomposition and blackening then taking place. The two preparations when mixed showed no depression of melting point. On analysis :

0.1124 gave 14.7 c.c. moist nitrogen at 16° and 750 mm. N = 15.04.

C₁₃H₉O₅N₃ requires N = 14.66 per cent.

The *ethyl ester* of this acid was prepared from both specimens in the usual manner. Each preparation melted at 220—225°, a certain amount of decomposition taking place.

0.1165 gave 14.3 c.c. moist nitrogen at 23° and 759 mm. N = 13.82.

C₁₅H₁₃O₅N₃ requires N = 13.33 per cent.

Both the *m*- and *p*-nitrobenzeneazosalicylic acids resist the action of dilute nitric acid to a greater degree than the unsubstituted acid. Attempts at nitration, even at 100°, led to the recovery of nearly the whole of the original acids in an unchanged condition.