

LXI.—*Bromination of Benzeneazophenol.*

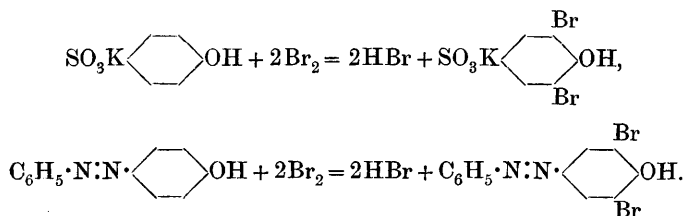
By J. T. HEWITT and W. G. ASTON.

RECENTLY, one of the authors of this communication (Trans., 1900, 77, 99) showed that when benzeneazophenol was nitrated with dilute nitric acid at a temperature of 40—45°, the dilution of the nitric acid being sufficient to preclude the formation of a salt from the acid and the azophenol in its tautomeric condition of quinonephenylhydrazone, one nitro-group entered into the ortho-position relatively to the hydroxyl group of the phenol nucleus, the substance behaving chemically as a true hydroxyl derivative of azobenzene. Such a reaction was hardly in accordance with Hantzsch's view that benzeneazophenol was a phenylhydrazone of quinone when in the free condition, and it was thought that the results so obtained formed at least as valid an argument for the phenolic formula as the contrary argument of Hantzsch, which, to a certain extent, was based on an incorrect determination of the dissociation constant for phenol (Hantzsch, *Ber.*, 1899, 32, 3069, 3082; Farmer and Hantzsch, *Ber.*, 1899, 32, 3089. Compare Walker, Trans., 1900, 77, 18; *Zeit. physikal. Chem.*, 1900, 32, 137).

Almost immediately after the appearance of this work, Professor Armstrong made a communication to the Society (Proc., 1899, 15, 243) in which he stated that although *p*-hydroxyazobenzene might be expected to be readily brominated in the ortho-position relatively to the hydroxyl group, it yields a product convertible into *p*-bromoaniline and phenol, and capable of being prepared from these substances, a result showing that towards bromine the substance brominated behaves as a hydrazone. Experiments on the bromination of benzeneazophenol had been undertaken in this laboratory last summer, but on account of the relative difficulty of regulating the reaction, were put aside until the nitration with dilute nitric acid had been studied and were resumed at once on the appearance of Prof. Armstrong's communication.*

* I received letters from Prof. Meldola and Prof. Auwers soon after the publication of Prof. Armstrong's note. Prof. Meldola told me that he had some few years

We found that when benzeneazophenol was dissolved in acetic acid, and sodium acetate added to prevent any liberation of hydrogen bromide—which as a strong mineral acid forms a salt of quinone phenylhydrazone—the first product of bromination was benzeneazo-*o*-dibromophenol, and not a monobromo-derivative. The reaction is, in fact, the complete analogue of that between potassium phenol-*p*-sulphonate and bromine; in the latter case, Senhofer (*Annalen*, 1870, 156, 103), when he used molecular proportions of the reacting compounds, obtained a mixture of unaltered substance and its dibromo-derivative. The two reactions may be represented by the similar equations,



At the risk of giving too much, rather than too little detail, we describe first the reaction when molecular proportions are employed, and afterwards the process adopted for obtaining benzeneazodibromophenol in quantity. Five grams of benzeneazophenol and 10 grams of crystallised sodium acetate were dissolved in 50 grams of hot glacial acetic acid, the solution was then cooled down to the ordinary temperature and violently agitated in a conical flask, whilst 4 grams of bromine in 20 grams of glacial acetic acid were run in drop by drop. The addition took 10 to 15 minutes, and at the end of the operation the temperature was 26°. After standing a further 10 minutes, the contents of the flask were poured into cold water, collected, washed, and distilled with steam; 0.02 gram of tribromophenol (m. p. 95°) separated from the aqueous distillate (about 600 c.c.). The residue in the flask was collected and fractionally recrystallised from glacial acetic acid. The first crop of crystals was twice recrystallised from

ago brominated benzeneazophenol in glacial acetic acid solution, adding sodium acetate. Under these conditions, he obtained an oily substance which he regarded as benzeneazo-*o*-bromophenol; he also recommended me to use sodium acetate to bind free hydrogen bromide, and very kindly left the rest of the work in my hands. I wish to tender my best thanks to Prof. Meldola for his kindness and advice, and to Prof. Auwers who had also undertaken the bromination of benzeneazophenol, but abandoned it on the appearance of the papers by Prof. Armstrong and myself. Prof. Auwers considered that it was very probable that Prof. Armstrong had been brominating a salt of quinonephenylhydrazone, as he had himself noticed that the first drop of bromine in a glacial acetic acid solution of benzeneazophenol produced a carmine-red precipitate.—J. T. HEWITT.

glacial acetic acid, and when washed and dried weighed 1.55 grams ; it melted at 135° (corr.). On analysis :

0.1102 gram gave 7.80 c.c. moist nitrogen at 18° and 746 mm. $N = 8.02$.

$C_{12}H_8ON_2Br_2$ requires $N = 7.88$ per cent.

From the united mother liquors, a second crop of crystals (0.56 gram), melting at about 127° (uncorr.), was obtained, and by successive additions of water two further crops, the first (0.59 gram) a mixture with a melting point of about 80° , the second (2.30 grams) consisting essentially of benzeneazophenol.

The identity of the purified first crop with benzeneazodibromophenol was proved by adding a diazotised solution of aniline to an alkaline solution of 2:6-dibromophenol, and allowing this to stand overnight. On the addition of hydrochloric acid, a tarry mass separated ; steam was blown through to remove unaltered dibromophenol, and the tarry residue repeatedly recrystallised from dilute spirit. This left most of the tar undissolved, and by stirring the solution as it cooled, orange needles were deposited. After several such recrystallisations, the substance was found to have the same melting point as the product obtained by the direct bromination of benzeneazophenol, and a mixture of the two preparations dissolved in benzene and evaporated also melted at the same temperature.

It may be mentioned that the yield of substance obtained in coupling phenyldiazonium chloride with alkaline dibromophenol is extremely small, most of the dibromophenol being recovered unchanged.

The process finally adopted in the preparation of benzeneazodibromophenol is to dissolve recrystallised benzeneazophenol (25 grams), together with its own weight of fused sodium acetate in 10 times its weight of glacial acetic acid (250 grams), then, after cooling below 10° , to run in, drop by drop, 32 grams of bromine, dissolved in 100 grams of glacial acetic acid, agitating vigorously the whole time, and taking care that the temperature does not rise. During the addition of the bromine, the substance separates out as yellow crystals ; to render the separation as complete as possible, final cooling to 0° is desirable, and in this way 27 grams of the dry product having the correct melting point were obtained. From the mother liquors, a further quantity of a slightly less pure substance may be recovered, making the total yield nearly quantitative. A great advantage of the process is that the acetic acid is neither diluted nor contaminated with hydrogen bromide, so that it is easily recovered by distillation. On recrystallisation of the benzeneazodibromophenol from benzene, it is obtained in beautiful, long, orange needles, which melt at 136° (corr.). On analysis :

0.1271 gave 0.1943 CO_2 and 0.0253 H_2O . $\text{C} = 41.12$; $\text{H} = 2.21$.

0.1751 „ 11.8 c.c. moist nitrogen at 10° and 760 mm. $\text{N} = 8.07$.

0.1989 „ 0.2109 AgBr . $\text{Br} = 45.12$.

$\text{C}_{12}\text{H}_8\text{ON}_2\text{Br}_2$ requires $\text{C} = 40.44$; $\text{H} = 2.27$; $\text{N} = 7.88$; $\text{Br} = 44.91$ percent.

Benzeneazo-*o*-dibromophenol is very soluble in acetone, and easily soluble in hot benzene, chloroform, ether, or ethyl acetate; glacial acetic acid and "methylated" spirit dissolve it sparingly in the cold, whilst it is nearly insoluble in light petroleum.

A benzene solution of benzeneazodibromophenol, although darkened in colour by hydrogen chloride, is not precipitated; if, however, the substance is intimately ground with strong sulphuric acid, a carmine-red mass, evidently a sulphate, is obtained. On treating this sulphate with water, it becomes yellow, forming a crystalline powder which, after drying in the air, has the melting point 134° (uncorr.). A hydrate had evidently not been produced by the treatment.

Hot caustic soda solution readily dissolves the azophenol, and a sodium salt separates in fine yellow needles on cooling. After drying at 110° until of constant weight, the compound was analysed:

0.2707 gave 0.0491 Na_2SO_4 . $\text{Na} = 5.88$.

$\text{C}_{12}\text{H}_7\text{ON}_2\text{Br}_2\text{Na}$ requires $\text{Na} = 6.08$ per cent.

An aqueous solution of this salt gives precipitates with salts of the heavy metals; it is noticeable that the barium salt is soluble in boiling water, and separates in yellow needles on cooling. This behaviour contrasts with that of barium benzeneazo-*o*-nitrophenolate which forms a nearly insoluble vermilion precipitate; the difference is perhaps due to the structure of the nitro-group.

The *acetyl* derivative, obtained by heating the phenol for 2 hours with 3 to 4 times its weight of acetic anhydride, crystallised from glacial acetic acid in yellow needles and melted at 143° .

0.1584 gave 0.1496 AgBr . $\text{Br} = 40.16$.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$ requires $\text{Br} = 40.17$ per cent.

The substance dissolved easily in acetone or chloroform, and moderately easily in benzene, ether, or ethyl acetate, but only sparingly in the other common organic solvents.

The *benzoyl* derivative, prepared by boiling benzeneazodibromophenol with 3 to 5 times its weight of benzoyl chloride for 20 to 30 minutes, crystallises from hot spirit in beautiful, orange leaflets melting at 120° (corr.). The only solvents which dissolve this substance at all easily in the cold are acetone, benzene, ether, and ethyl acetate; it requires about 50 times its weight of boiling spirit, or over 200 times its weight of cold spirit, for solution.

0.1310 gave 7.1 c.c. moist nitrogen at 18° and 746 mm. $\text{N} = 6.14$.

$\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}_2$ requires $\text{N} = 6.11$ per cent.

Ethyl Ether.—None of the other derivatives prepared showing any instability of the bromine atoms, the examination of the ethyl derivative promised especial interest on account of Prof. Armstrong's statement that benzeneazo-*o*-bromophenetole easily loses bromine when dissolved in acetone. The ethyl ether was prepared by adding a mixture of 2 grams of ethyl bromide and 3 grams of absolute alcohol to 3 grams of the sharply dried and finely powdered sodium salt contained in a small bottle. This was tightly corked and shaken, the salt dissolved at once, and almost immediately small crystals of sodium bromide began to make their appearance. The reaction was completed by heating for 45 minutes to 100°; after cooling, the contents of the bottle were poured into warm dilute caustic soda, the oil which separated subsequently solidifying. The substance was washed repeatedly, and finally recrystallised from dilute spirit, silky, yellowish-orange needles melting at 71° (corr.) being obtained.

0.1215 gave 7.80 c.c. moist nitrogen at 12° and 752 mm. $N = 7.54$.
 $C_{14}H_{12}ON_2Br_2$ requires $N = 7.31$ per cent.

This ethyl ether is dissolved easily by most organic solvents, especially by acetone and ether; it is, however, only sparingly soluble in light petroleum.

From Prof. Armstrong's statement, it might be expected that this substance would react with acetone; in fact, with bromine atoms on either side of the ethoxyl group, an even greater reactivity might be expected than in the case of benzeneazo-*o*-bromophenetole. After boiling for 1 hour with acetone and then evaporating the solvent, no smell of bromoacetone was detected; the residue—which crystallised beautifully—was found to contain bromine, to melt at the original temperature, and when mixed with a portion of the analysed sample, which had not been treated in this manner, to be without influence on its melting point. The only conclusion to be drawn is that benzeneazodibromophenetole is unchanged by acetone under the conditions mentioned.

Although, when a substance exhibits tautomerism, it is only natural to expect that both configurations will be represented in any specimen, the vastly preponderating quantity of benzeneazophenol consists of the phenolic modification, both bromination and nitration experiments leading to the same conclusion. The results thus obtained coincide with those deduced from physical measurements by Auwers. Further experiments are in progress in this laboratory, the results so far obtained confirming those already published.

EAST LONDON TECHNICAL COLLEGE,