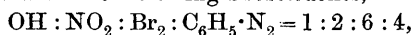


XXV.—*Action of Bromine on Benzeneazo-o-nitrophenol.*

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IN several earlier communications it has been shown that when benzeneazophenol and allied compounds are treated with dilute nitric acid or with bromine in presence of sodium acetate, substitution takes place in the ortho-position to the phenolic hydroxyl. Typical cases are the production of benzeneazo-*o*-nitrophenol (Hewitt, Trans., 1900, 77, 49) and of benzeneazo-*o*-*o*-dibromophenol (Hewitt and Aston, Trans., 1900, 77, 712, 810) under the conditions mentioned. It is, however, noticeable that whereas only one nitro-group is introduced, it has been found impossible to isolate such a compound as benzeneazo-*o*-bromophenol, even when only one molecular proportion of bromine has been employed, a mixture of the unaltered azophenol and its dibromo-derivative resulting.

Whilst it appeared very probable that, if benzeneazo-*o*-nitrophenol were subsequently brominated in presence of sodium acetate, a mono-bromo-derivative with the following substituents,



would be produced, no direct proof had been furnished, and the result appeared to be even somewhat doubtful when, on trying the experiment, a compound was obtained melting at 154·5° (corr.), practically the same melting point as that obtained by H. V. Mitchell with a product obtained from diazotised *p*-bromoaniline and *o*-nitrophenol. The two substances were, however, found to depress one another's melting points, and we are now in a position to give the definite proof that bromination really took place in the other free ortho-position (relatively to the phenolic hydroxyl).

Preparation of 4-Benzeneazo-2-bromo-6-nitrophenol.

The benzeneazo-*o*-nitrophenol was prepared according to the method previously described (Trans., 1900, **77**, 49), but the purification was considerably facilitated by taking advantage of the insolubility of the barium salt. The crude nitration product was dissolved in excess of hot dilute ammonia and barium chloride solution added, the red precipitate was collected at the pump and well washed with hot water until the filtrates were of a light shade. By decomposition with dilute hydrochloric acid and recrystallisation from glacial acetic acid, the benzeneazo-*o*-nitrophenol can be obtained with the correct melting point. In fact, the well-washed barium salt furnishes directly on decomposition with acid a substance melting within two or three degrees of the correct temperature, and usually this product has been employed in further experiments.

Benzeneazo-*o*-nitrophenol is dissolved in four times its weight of boiling glacial acetic acid, together with half its weight of fused sodium acetate. The solution is cooled down to the ordinary temperature under continual stirring, whereby a thin paste is produced. The molecular proportion of bromine diluted with twice its weight of glacial acetic acid is then added with continual stirring and external cooling. Usually rather more acetic acid has to be added after two-thirds of the bromine has been introduced owing to the thickening of the mixture. The resulting mass is treated with hot water and collected at the pump, the crude product usually melting at about 140—145°. By two recrystallisations from boiling glacial acetic acid, the substance is obtained in small yellow needles melting at 154·5—155°.

0·1379 gave 0·2259 CO₂ and 0·0368 H₂O. C = 44·68; H = 2·42.

0·1254 „ 14·4 c.c. nitrogen at 19° and 763 mm. N = 13·47.

0·0899 „ 0·0520 AgBr. Br = 24·39.

C₁₂H₈O₃N₃Br requires C = 44·70; H = 2·51; N = 13·07; Br = 24·82
per cent.

The substance is readily soluble in acetone and boiling glacial acetic acid, but only moderately in alcohols and aromatic hydrocarbons. The solubility in pyridine is accompanied by salt formation, the solution leaving on evaporation an orange powder melting at 112°. This azophenol gives no hydrochloride. If hydrogen chloride is led into its benzene solution, a slight separation of the unchanged azophenol occurs, but no salt formation can be detected.

Constitution of the Benzeneazobromonitrophenol.

Many experiments were initiated having for their object the determination of the position of the bromine atom. Attempts at reduction with isolation of the resulting diaminobromophenol as tribenzoyl derivative failed on account of the elimination of the bromine.

The appearance of the recent paper by Otto Schmidt (*Ber.*, 1905, **38**, 3021; compare Meldola and Morgan, *Trans.*, 1889, **55**, 603) led to the trial of strong nitric acid as an agent of fission. Two grams of the azophenol were added in small quantities at a time to 20 grams of nitric acid (sp. gr. 1.5) cooled externally by ice. The dark red solution was poured off after five to seven minutes on to crushed ice, the precipitate collected at the pump, and the filtrate added to an ice-cold solution of 1.5 grams of β -naphthol and 15 grams of sodium hydroxide in 200 c.c. of water. A dark red precipitate was formed, which was collected, washed with boiling water, and dried.

The first precipitate obtained by pouring the nitric acid solution on to ice weighed 1.5 grams, and, without recrystallisation, melted at 116° (uncorr.). When mixed with 2-bromo-4:6-dinitrophenol (m. p. 118°, Körner, *Jahresber.*, 1875, 337), the melting point was not depressed. Theoretically, 1.6 grams of bromodinitrophenol should have been obtained.

The product obtained by coupling the simultaneously produced diazonium salt with β -naphthol, which weighed 1.2 grams, melted in the crude condition at 237° (uncorr.) and at 239° (= 246° corrected) after recrystallisation from toluene. Its identification with *p*-nitrobenzeneazo- β -naphthol was completed by a nitrogen estimation and a determination of melting point after mixture with synthesised *p*-nitrobenzeneazo- β -naphthol.

0.1345 gave 16.3 c.c. N at 12° and 759 mm. $N = 14.48$.

$C_{16}H_{11}O_3N_3$ requires $N = 14.37$ per cent.

The result leaves no doubt as to the position of the bromine atom, which must have entered into the ortho-position to the phenolic hydroxyl.

The sodium salt separates from hot solutions in very small crystals fairly soluble in water; the salt was analysed after drying over sulphuric acid in a vacuum for three days.

0.2079 gave 0.0453 Na_2SO_4 . $Na = 7.06$.

$C_{12}H_7O_3N_3BrNa$ requires $Na = 6.81$ per cent.

The potassium salt forms small, extremely dark-coloured prisms.

0.0810 gave 0.0182 K_2SO_4 . $K = 10.07$.

$C_{12}H_7O_3N_3BrK$ requires $K = 10.88$ per cent.

The *ammonium* salt, which has not been isolated for analysis, is apparently only sparingly soluble in cold water.

An ammoniacal solution of the azophenol gives precipitates with many metallic salt solutions.

Metallic salt.	Precipitate.	Metallic salt.	Precipitate.
Silver nitrate	Orange-red, insoluble.	Stannous chloride..	Brown precipitate, soluble in hot water.
Copper sulphate ...	Yellow.	Lead acetate.....	Reddish-brown precipitate, insoluble on boiling.
Barium chloride ...	Orange-red, soluble in boiling water.	Manganous chloride	Brick-red, soluble on boiling.
Magnesium sulphate	Orange, soluble in hot water.	Ferrous sulphate ...	Yellow.
Zinc sulphate	Orange.	„ chloride ...	Colloidal.
Mercuric chloride...	Yellow.	Cobalt nitrate	Light brown.
Ammonia alum.....	Yellow cloudiness in cold solution, yellowish-brown precipitate on boiling.	Nickel sulphate ...	Brick-red, insoluble in hot water.

The *acetyl* derivative, $C_6H_5 \cdot N : N \cdot C_6H_2Br(NO_2) \cdot O \cdot CO \cdot CH_3$, was prepared by boiling the substance with its own weight of fused sodium acetate and four times its weight of acetic anhydride for five hours in a reflux apparatus. The product was isolated in the usual manner and recrystallised from glacial acetic acid, when dark red needles (m. p. 137°) were obtained.

0.1679 gave 0.2862 CO_2 and 0.0434 H_2O . $C = 46.49$; $H = 2.86$.

0.2329 „ $H \cdot C_2H_3O_2$ requiring 6.2 $N/10$ NaOH. $C_2H_3O = 11.44$.

$C_{14}H_{10}O_4N_3Br$ requires $C = 46.13$; $H = 2.77$; $C_2H_3O = 11.82$ per cent.

The *benzoyl* derivative, $C_6H_5 \cdot N : N \cdot C_6H_2Br(NO_2) \cdot O \cdot CO \cdot C_6H_5$, was produced by gently boiling the substance with three times its weight of benzoyl chloride for two hours in a reflux apparatus. The product was poured into 80 per cent. alcohol, and the precipitate, when hard, collected and recrystallised from toluene. Radiating brown aggregates of needles were obtained which melted at 131° .

0.1447 gave 0.2849 CO_2 and 0.0417 H_2O . $C = 53.7$; $H = 3.2$.

$C_{19}H_{12}O_4N_3Br$ requires $C = 53.5$; $H = 2.8$ per cent.

4-p-Tolueneazo-2-bromo-6-nitrophenol.—To control the foregoing result, the action of bromine on *p*-tolueneazo-*o*-nitrophenol (Hewitt and Lindfield, Trans., 1901, 79, 156) was also studied. Again it was found that the free ortho-position to the phenolic hydroxyl group was attacked with formation of the above-mentioned substance. We discovered that a slip had occurred in the earlier paper, the melting point of *p*-tolueneazo-*o*-nitrophenol being given as 147° , when, as a

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matter of fact, it is 174° . In these circumstances, the purity of our product was controlled by analysis.

0.1578 gave 0.3521 CO_2 and 0.0624 H_2O . $\text{C} = 60.9$; $\text{H} = 4.4$.

$\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_3$ requires $\text{C} = 60.7$; $\text{H} = 4.3$ per cent.

The azonitrophenol and half its weight of fused sodium acetate were dissolved in eight parts by weight of glacial acetic acid. A molecular proportion of bromine dissolved in about twice its weight of acetic acid was added under previously mentioned precautions; after dilution with water, the product was collected and washed with hot water. Acetic acid is not suitable for purification, as any unattacked azonitrophenol is not removed by recrystallisation from this solvent. Two recrystallisations from ethyl acetate furnish fine orange needles melting sharply at 161° .

0.0975 gave 0.1666 CO_2 and 0.0294 H_2O . $\text{C} = 46.6$; $\text{H} = 3.4$.

$\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_3\text{Br}$ requires $\text{C} = 46.4$; $\text{H} = 3.0$ per cent.

The position of the bromine atom was determined by decomposition with fuming nitric acid, when 2-bromo-4 : 6-dinitrophenol melting at 118° was obtained.

The *acetyl* derivative, $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$, was prepared in the usual manner, and after recrystallisation from ethyl acetate formed orange needles melting at 124° .

0.0934 gave 0.1646 CO_2 and 0.0279 H_2O . $\text{C} = 48.1$; $\text{H} = 3.3$.

$\text{C}_{15}\text{H}_{12}\text{O}_4\text{N}_3\text{Br}$ requires $\text{C} = 47.7$; $\text{H} = 3.2$ per cent.

The *benzoyl* derivative, obtained from the azophenol by boiling in a reflux apparatus with five times its weight of benzoyl chloride, excess of which was destroyed by alcohol, crystallised from ethyl acetate in small, yellowish-orange crystals melting at 129° .

0.1102 gave 0.2203 CO_2 and 0.0338 H_2O . $\text{C} = 54.5$; $\text{H} = 3.4$.

$\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_3\text{Br}$ requires $\text{C} = 54.5$; $\text{H} = 3.2$ per cent.

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