CXX.—*The Action of Substituting Agents on Benzene-azo- β -Naphthol.*

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THE authors recently communicated the results they had obtained in studying the action of bromine on benzeneazo- α -naphthol, and now describe the action of bromine as well as of nitric acid on benzeneazo- β -naphthol.

Some years ago, Margary (*Gazzetta*, 1883, 13, 438) added bromine in molecular proportion to a solution of benzeneazo- β -naphthol in glacial acetic acid; the product obtained melted at 160—161° and

was recognised as *p*-bromobenzeneazo- β -naphthol from the fact that *p*-bromoaniline was obtained on reduction with stannous chloride and hydrochloric acid. As has frequently happened in cases of this sort, no precautions were taken to avoid the influence of mineral acids, and it was thus of interest to repeat the bromination with addition of sodium acetate, as well as to study the action of nitric acid of various concentrations.

Action of Nitric Acid.

Action of Nitric Acid of sp. gr. 1.15.—Two grams of benzeneazo- β -naphthol were added to an excess of nitric acid (sp. gr. 1.15). Apparently no change took place in the cold; the mixture was then heated over wire gauze until a vigorous reaction set in, when the flame was withdrawn. The reaction being finished, excess of cold water was added, the solid residue collected, and washed free from nitric acid. After drying and recrystallisation from benzene, a brownish-red powder was obtained melting at about 168°, and obviously consisting of a mixture of substances. The powder proved to be for the greater part soluble in hot dilute sodium hydroxide solution; on cooling, a sodium salt separated in such quantity as to form a thick, crystalline paste. The crystals were collected, again recrystallised from hot water, and decomposed with hydrochloric acid. The substance obtained melted at 191° (uncorr.) after recrystallisation from hot glacial acetic acid, from which solvent it was deposited as small, pale yellow needles:

0.1479 gave 15.4 c.c. nitrogen at 19° and 745 mm. $N = 11.90$.

$C_{10}H_6O_5N_2$ requires $N = 11.99$ per cent.

The identity of the compound with 1:6-dinitro- β -naphthol, $C_{10}H_5(NO_2)_2 \cdot OH$, was fully established by the fact that when mixed with a specimen of this substance it did not depress its melting point.

The small residue left after extraction with sodium hydroxide was bright red in colour, and after recrystallisation from glacial acetic acid melted at 241–242° (uncorr.); its identity with *p*-nitrobenzeneazo- β -naphthol was established by the fact that when mixed with the synthetical product no depression of melting point could be observed.

A repetition of the nitration with acid of sp. gr. 1.15 resulted in the production of 0.5 gram of *p*-nitrobenzeneazo- β -naphthol and 1.6 grams of dinitronaphthol from 2 grams benzeneazo- β -naphthol. The weights refer to crude products; recrystallisation from benzene was omitted. Practically the whole of the azonaphthol employed is accounted for, about one-fifth of the benzeneazo- β -naphthol employed being nitrated in the benzene nucleus, whilst the other four-fifths are attacked in the naphthol nucleus, the benzeneazo-group in position 1

being replaced by the nitro-group, whilst substitution also takes place in position 6.

This result is, however, not inconsistent with initial nitration in the benzene nucleus and subsequent destruction of the nitrobenzeneazo-group. To test the possibility of this explanation, 2 grams of *p*-nitrobenzeneazo- β -naphthol were heated for some time with an excess of dilute nitric acid of sp. gr. 1.15. On treatment of the product with sodium hydroxide solution in the manner already indicated, it was found that most of the *p*-nitrobenzeneazo- β -naphthol remained unattacked, and only a small quantity of the 1:6-dinitro- β -naphthol was obtained. The resistance displayed by this nitro-substituted azo-compound towards the action of dilute nitric acid compared with the readiness with which the parent benzeneazonaphthol is attacked, shows that 1:6-dinitro- β -naphthol must be looked on as a primary product of the action of dilute nitric acid on the latter substance.

Action of a Mixture of Concentrated Nitric and Sulphuric Acids.—Nitric acid added to a solution of benzeneazo- β -naphthol in excess of concentrated sulphuric acid, converts the substance nearly quantitatively into *p*-nitrobenzeneazo- β -naphthol. Two grams of benzeneazo- β -naphthol were made into a paste with 20 c.c. of concentrated sulphuric acid, and 0.76 gram of nitric acid (sp. gr. 1.4) mixed with concentrated sulphuric acid gradually added, the mixture being cooled and well stirred. After standing overnight, the mixture was poured into water and the precipitate collected, washed, and dried. The weight of substance obtained was 2.30 grams. Replacement of one hydrogen atom by one nitro-group should have given 2.36 grams.

To ascertain how far the product consisted of *p*-nitrobenzeneazo- β -naphthol, it was warmed with dilute sodium hydroxide solution; the residue weighed 1.78 grams and melted at 234°, but after recrystallisation from glacial acetic acid, the melting point was 239° (uncorr.). The hot alkaline filtrate deposited solid matter to the extent of 0.14 gram on cooling; this was not a sodium salt, but melted in the crude condition at 221°, and after recrystallisation at 239° (uncorr.), the substance did not depress the melting point of *p*-nitrobenzeneazo- β -naphthol. On acidification, the final filtrate deposited a tarry mass which was disregarded.

Action of Bromine.

In Absence of Sodium Acetate.—The bromination of benzeneazo- β -naphthol has been studied by various chemists. Typke (*Ber.*, 1877, 10, 1550) stated that bromine entered the naphthalene nucleus; the result was contradicted by Margary (*Gazzetta*, 1883, 13, 438), who obtained a substance melting at 160–161° which furnished *p*-bromoaniline on reduction. Margary concluded that the substance produced

was *p*-bromobenzeneazo- β -naphthol, a result confirmed by Zincke and Bindewald (*Ber.*, 1884, 17, 3032), who, however, gave the melting point as 167—168°. Finally, Bamberger synthesised *p*-bromobenzeneazo- β -naphthol from *p*-nitrosobromobenzene, β -naphthol, and hydroxylamine, giving the melting point as 172—173° (*Ber.*, 1895, 28, 1222).

We find that if finely powdered benzeneazo- β -naphthol be suspended in ten times its weight of glacial acetic acid and brominated in the cold with the calculated quantity of bromine dissolved in acetic acid, *p*-bromobenzeneazo- β -naphthol is obtained in practically quantitative amount; after recrystallisation, the substance melts at 170° (uncorr.). The identity of the substance was confirmed by mixing with the synthetic compound, when no depression of melting point was observed. The formation of *p*-bromoaniline on reduction was also put beyond doubt by distilling the reduction mixture, after rendering alkaline, in a current of steam, and benzoylating the base contained in the distillate. The recrystallised benzoyl derivative contained bromine and melted at 200° (uncorr.).

In Presence of Sodium Acetate.—Experiments were next made on the action of bromine in presence of sodium acetate. At the ordinary temperature, bromine appears to be without action on a solution of benzeneazo- β -naphthol in glacial acetic acid if sodium acetate has been added. Even on boiling, reaction, if it takes place at all, is extremely limited. At 165—170° under pressure, the bromine is used up in half-an-hour. On pouring into cold water the product of the action of 3·5 grams of bromine on 5 grams of benzeneazo- β -naphthol dissolved together with 3·5 grams of fused sodium acetate in 50 c.c. of glacial acetic acid, a brown tar was deposited which liquefied completely below 100°. Attempts to separate the mass into its constituents were extremely unsatisfactory; a small quantity of a crystalline powder was obtained on one occasion by dissolving the mass in ethyl acetate and adding acetic acid, the excess of ethyl acetate being removed by distillation. The substance melted at about 260° (uncorr.) and contained bromine:

0·0818 gave 0·1936 CO₂ and 0·0261 H₂O. C = 65·8; H = 3·5.

0·0810 „ 0·0231 AgBr. Br = 12·1.

0·1068 „ 0·0308 AgBr. Br = 12·3 per cent.

The substance is evidently not a monobromobenzeneazo- β -naphthol, which would require 24·4 per cent. of bromine; probably it is formed by the condensation of 2 mols. of the azo-compound. The quantity of the substance produced is so extremely small, that, whatever its structure, it can have but little bearing on the constitution of benzeneazo- β -naphthol.

Bromobenzeneazo- β -naphthols.

During the progress of the work described above, the three bromobenzeneazo- β -naphthols were prepared for purposes of comparison, and further characterised by conversion into acetyl or benzoyl derivatives.

o-Bromobenzeneazo- β -naphthol was prepared in the customary manner; it melts at 165°. It is best obtained by recrystallisation from boiling benzene, from which it is deposited as small, brownish plates; it dissolves easily in carbon disulphide, and is taken up fairly readily by acetic acid, acetone, ethyl acetate, ether, or light petroleum. Its solubility in alcohol is slight:

0.1472 gave 0.0847 AgBr. Br = 24.49.

$C_{16}H_{11}ON_2Br$ requires Br = 24.43 per cent.

The *acetyl* derivative separates from glacial acetic acid as small, brown crystals with a bronzy lustre and melts at 157°:

0.1368 gave 0.0698 AgBr. Br = 21.94.

$C_{18}H_{13}O_2N_2Br$ requires Br = 21.69 per cent.

m-Bromobenzeneazo- β -naphthol, recrystallised from benzene, forms broad, red needles exhibiting a beautiful reflex; it melts at 172°:

0.2239 gave 17.0 c.c. nitrogen at 20° and 737 mm. N = 8.61.

0.2460 „ 0.1414 AgBr. Br = 24.22.

$C_{16}H_{11}ON_2Br$ requires N = 8.59; Br = 24.43 per cent.

The *acetyl* derivative melts at 88° after recrystallisation from glacial acetic acid:

0.3012 gave 20.5 c.c. nitrogen at 20° and 759 mm. N = 7.72.

$C_{18}H_{13}O_2N_2Br$ requires N = 7.48 per cent.

The *benzoyl* derivative is a beautiful, dark red substance, crystallising in obliquely terminated prisms and melts at 159°:

0.2176 gave 12.0 c.c. nitrogen at 22° and 770 mm. N = 6.45.

$C_{23}H_{15}O_2N_2Br$ requires N = 6.49 per cent.

p-Bromobenzeneazo- β -naphthol has already been described; the melting point we observed for the substance agreed with that given by Bamberger.

The *acetyl* derivative forms beautiful, dark red needles and melts at 136°:

0.1784 gave 0.3813 CO₂ and 0.0598 H₂O. C = 58.29; H = 3.68.

$C_{18}H_{13}O_2N_2Br$ requires C = 58.53; H = 3.52 per cent.

THE CONDENSATION OF DIMETHYLAMINOBENZALDEHYDE. 1207

The *benzoyl* derivative melts at 157° , and separates from glacial acetic acid as very dark red needles :

0.2344 gave 0.1012 AgBr. Br = 18.41.

$C_{23}H_{15}O_2N_2Br$ requires Br = 18.05 per cent.

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