

XVII.—*Researches on the Constitution of Azo- and Diazo-derivatives.*  
 V. *Compounds of the Naphthalene  $\beta$ -Series*—continued.

By RAPHAEL MELDOLA, F.R.S., and GILBERT T. MORGAN.

IN the last paper referring to the present branch of investigation (Trans., 1888, 460; Meldola and East), it was shown that the azo-derivatives of  $\beta$ -naphthol contain an atom of hydrogen capable of being displaced by acid radicles, a property which they share in common with their  $\alpha$ -analogues (Zincke and Bindewald, *Ber.*, 1884, 3030). Of the alkyl-derivatives of the azo- $\beta$ -naphthol compounds, the only representative at present known is the benzeneazo- $\beta$ -naphthyl ether of Weinberg (*Ber.*, 1887, 3171). The importance, from a theoretical point of view, of ascertaining whether this displaceable hydrogen-atom of the azo- $\beta$ -naphthol compounds is attached to the oxygen or to the nitrogen of the azo-group has from time to time been pointed out in the course of the present series of researches, and has recently been emphasized in a paper read by one of the authors at the Bath meeting of the British Association (*Phil. Mag.*, 1888, 403). The present paper contains the results of experiments undertaken with the object of throwing further light on this question.

I. *Benzoyl-derivatives of Azo- $\beta$ -Naphthol Compounds.*

Acetyl-derivatives of azo- $\beta$ -naphthol compounds can be prepared, as pointed out in the last paper, by two distinct methods. If the radicle attached to the azo-group is more or less of an acid character, such as nitrophenyl,  $C_6H_4NO_2$  (*p* or *m*), the corresponding  $\beta$ -naphthylamine azo-compound is attacked by nitrous acid in the presence of glacial acetic acid, with the formation of the azo-naphthyl acetate (*loc. cit.*, p. 465).<sup>\*</sup> This method does not appear to be applicable

<sup>\*</sup> The formation of phenylic acetates from the corresponding amines, by means of the diazo-reaction in the presence of glacial acetic acid, was made known in a paper communicated to the Chemical Society of Germany on January 24th, 1888 (*Ber.*, 1888, 601), and in a subsequent paper read to this Society (Trans., May, 1888, 465), it was stated that "as the reaction promises to be widely applicable for the synthesis of phenylic acetates and other ethereal salts, it is proposed to extend the investigation in this direction, and to make a special study of the conditions which determine the displacement of amidogen by the  $C_2H_5O-O$ -group by means of the diazo-reaction." Notwithstanding the publicity thus given to the method, and the explicit claim to continue its further investigation, a paper appeared in the *Amer. Chem. Jour.* of last September (10, 368) by W. R. Orndorff, containing the results of the application of this reaction for the formation of phenyl, cresyl, and

when the radicle attached to the azo-group is not acid, such as phenyl or naphthyl,  $C_6H_5$ ,  $C_{10}H_7$ , &c., in the azo- $\beta$ -naphthylamine compounds. In such cases, however, azo- $\beta$ -naphthyl acetates can be prepared by the direct acetylation of the azo- $\beta$ -naphthol compounds by means of sodium acetate and acetic anhydride, and the same method is generally applicable, whatever may be the nature of the radicle associated with the azo-group. The same remarks apply to the benzoyl-derivatives of azo- $\beta$ -naphthol compounds, some of which have been prepared by both methods in the manner described below.

*Benzeneazo- $\beta$ -Naphthyl Benzoate*,  $C_6H_5 \cdot N_2 \cdot C_{10}H_6 \cdot OC_7H_5O(\beta)$ .

This compound cannot be prepared by fusing benzeneazo- $\beta$ -naphthylamine with excess of benzoic acid, and adding the calculated quantity of sodium nitrite to the mixture: complete decomposition takes place under these circumstances with the formation of tarry products. A mixture of benzeneazo- $\beta$ -naphthol with dry sodium benzoate and benzoic anhydride, if heated for some hours to the fusing point of the anhydride, gives only a small yield of the azo- $\beta$ -naphthyl benzoate, owing to the difficulty of keeping the mixture in a homogeneous fluid condition, and to the continuous loss of anhydride by sublimation. After many partially successful attempts with benzoyl chloride, the following method was found to give perfectly satisfactory results:—

Benzeneazo- $\beta$ -naphthol is mixed with about an equal weight of dry and finely powdered sodium benzoate, and the mixture is then made just pasty with benzoyl chloride. The flask containing the mixture is fitted with a cork perforated for the reception of a tube drawn out to a fine point, and heat is applied by immersing the flask in boiling water.\* The reaction commences immediately on the application of heat, and is complete in about an hour, when the product is repeatedly extracted with hot water as long as benzoic acid is dissolved out. The contents of the flask fuse to a dark reddish oil under boiling water, a property which facilitates the washing operations, as the oil and hot water can be thoroughly mixed by agitation, and the former rapidly subsides to the bottom of the flask on allowing the contents to remain at rest for a few minutes. The benzoyl-derivative is easily decomposed by

other acetates from aniline, toluidine, &c. The investigation of the method has been going on in my laboratory since the beginning of last year, and these and other acetates and benzoates had been prepared from the diazo-salts of the corresponding amines before the appearance of the paper by the author referred to.—R. M.

\* At higher temperatures the reaction takes a different course; tarry products are formed which have not been further investigated.

ammonia, even when the latter is very dilute, so that it is unsafe to attempt to shorten the washing by the use of ammonia. In some of our first preparations, unaltered benzeneazo- $\beta$ -naphthol was always found, and this was afterwards traced to the use of ammonia in the washing waters. Sodium or ammonium carbonate also readily hydrolyse the benzoyl-derivative, and it is evident that the benzoyl-group is much more readily removed from this compound than is the acetyl from benzeneazo- $\beta$ -naphthyl acetate. When completely washed, the substance is crystallised from boiling alcohol, in which it dissolves readily. A specimen was further purified for analysis by dissolving in chloroform, in which it freely dissolves in the cold, and allowing the solvent to evaporate spontaneously in an open dish. The substance forms dense, orange-red crystals melting at 125°.

0.1025 gram gave 0.2951 gram CO<sub>2</sub> and 0.0438 gram H<sub>2</sub>O.

0.0894 gram burnt in a vacuum with CuO gave 5.9 c.c. moist N at 13° C., and 770.1 mm. bar.

|         | Calculated for<br>H <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> . | Found. |
|---------|---|--------|
| C ..... | 78.41   | 78.52  |
| H ..... | 4.55  | 4.74   |
| N ..... | 7.95  | 7.90   |

*Metanitrobenzeneazo- $\beta$ -Naphthyl Benzoate,*  
(*m*)NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·OC<sub>7</sub>H<sub>5</sub>O( $\beta$ ).

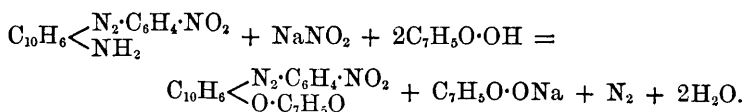
Metanitrobenzeneazo- $\beta$ -naphthylamine (m. p. 182°) is fused with excess of benzoic acid, and the calculated quantity of dry sodium nitrite added in small portions to the fused mixture. Nitrogen is freely given off, and when all the nitrite has been added, the product is washed with hot water till free from benzoic acid. The washing may in this case be accelerated by the use of dilute ammonia without fear of decomposition. The washed product is crystallised from hot glacial acetic acid, in which it is not very soluble, and finally from boiling alcohol, in which it dissolves only very sparingly, separating on cooling in the form of dull, reddish-orange, silky needles. The melting point is 171°. The following results were obtained on analysis :—

0.1676 gram gave 0.4280 gram CO<sub>2</sub> and 0.0612 gram H<sub>2</sub>O

0.2196 gram burnt in a vacuum with CuO gave 19.8 c.c. moist N at 17° C. and 761.7 mm. bar.

|         | Calculated for<br>C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> . | Found. |
|---------|---|--------|
| C ..... | 69.52   | 69.64  |
| H ..... | 3.77  | 4.05   |
| N ..... | 10.57   | 10.48  |

The substance is formed in this process according to an action perfectly similar to that which gives rise to the production of the acetate.



The benzoate may also be prepared by direct benzylation, and this method is much more convenient when the compound is required in quantity. For this purpose, metanitrobenzeneazo- - naphthol (m. p. 194°) is mixed with about its own weight of dry powdered sodium benzoate, and enough benzoyl chloride added to make the mixture into a paste. The contents of the flask are then kept just at the boiling point of the benzoyl chloride for 4—5 hours. The product is washed with dilute ammonia, and purified by crystallisation in the manner already described.

## II. *Reduction of Azo-β-Naphthol-derivatives containing Acid Radicles.*

In order to see whether any information concerning the position of the displaceable hydrogen-atom could be derived from a study of the products of reduction of the acetyl and benzoyl-derivatives, these compounds were reduced with tin and hydrochloric acid and with stannous chloride under various conditions.

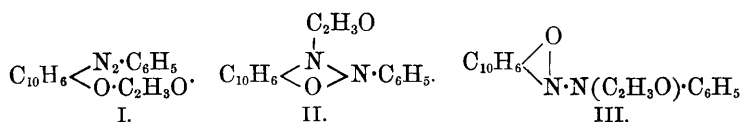
### *Reduction of Benzeneazo-β-Naphthyl Acetate.*

An alcoholic solution of the above compound is soon decolorised if boiled with tin and hydrochloric acid. On distilling off the alcohol and filtering to remove tarry impurities, the filtrate on standing gradually deposits a white curdy substance, which under the microscope is seen to consist of agglomerations of white needles. The addition of strong hydrochloric acid to the solution promotes the deposition of the white compound. The latter was therefore purified by being collected, dissolved in hot water, filtered, and reprecipitated by the addition of strong hydrochloric acid, this treatment being repeated till the substance dissolved without leaving any residue. The white substance thus obtained proved to be the hydrochloride of a mixture of bases. Many specimens were prepared and analysed without any concordant results being obtained; all attempts to separate the mixture into its constituents by fractional crystallisation or by conversion into other salts were unsuccessful. The free bases could not be isolated owing to their extremely oxidisable character. This product on reduction contains a considerable quantity of α-amido-β-naph-

thol, the presence of the latter compound being shown by the formation of  $\beta$ -naphthaquinone on oxidation by ferric chloride.

In spite of the unfavourable results obtained in our first experiments, the reduction was repeated, an alcoholic solution containing the theoretical quantity of stannous chloride being gradually mixed with a slightly warm alcoholic solution of the substance. After the mixture had stood for some hours, the alcohol was distilled off, and the product treated as above. The same white hydrochlorides were obtained, but the substance was evidently a mixture, and  $\alpha$ -amido- $\beta$ -naphthol was identified as one of its constituents as before. The analyses showed that in this case the mixture contained different proportions of the bases from those present in the product formed by violent reduction with tin and hydrochloric acid. In both series of experiments, the filtrate, after the removal of the white hydrochlorides first deposited, was treated with sulphuretted hydrogen in order to remove tin, and after the removal of the stannous sulphide the filtrate was evaporated to a small bulk, made alkaline with caustic soda, and submitted to steam distillation, when a considerable quantity of aniline was obtained, showing that this base is one of the products of reduction.

According to the current hypotheses of the constitution of the azo- $\beta$ -naphthol compounds, the acetyl-derivative of benzeneazo- $\beta$ -naphthol may have one of the following formulæ:—



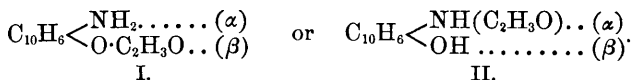
The first of these is what may be called the old formula, the second is that proposed by Liebermann, and the third is Zincke's, that is, the hydrazone formula.

Supposing the compound to be capable of complete reduction without the elimination of acetyl, these three compounds might be expected to yield the following products:—

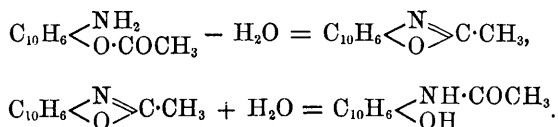
- I. Aniline and  $\alpha$ -amido- $\beta$ -naphthyl acetate.
- II. Aniline and  $\alpha$ -acetamido- $\beta$ -naphthol.
- III. Acetanilide and  $\alpha$ -amido- $\beta$ -naphthol.

We may state at once that a most careful search for acetanilide in the product of reduction has led to negative results. If the acetyl were attached to the nitrogen-atom it is improbable that this group would be removed under the conditions of reduction, since acetanilide is well known to be a stable compound under such circumstances. The third formula appears therefore to be inadmissible, and the

decision rests between Nos. I and II.\* A complication of the question, however, here arises from the possibility of intramolecular migration of the acetyl. Thus, according to the formulæ, the naphthalene portion of the molecule ought to give on complete reduction—



The investigations of Böttcher (*Ber.*, 1883, 1933) have shown that such a compound as No. I is incapable of existence, as it immediately becomes transformed into No. II. This was proved by preparing the acetyl-derivative of  $\alpha$ -nitro- $\beta$ -naphthol and reducing the latter, when a phenolic substance, viz., acetamido- $\beta$ -naphthol, was obtained instead of the basic amido- $\beta$ -naphthyl acetate. The acetyl-group accordingly becomes transferred from the oxygen to the nitrogen, probably through the intermediate formation of the anhydro-base and hydration of the latter :—



Whichever of the formulæ (I or II) be the correct one, it might therefore be expected that extreme reduction would give rise to the same acetamido- $\beta$ -naphthol. The latter is a perfectly stable phenolic substance melting, according to Böttcher, at 225°. It does not appear to be present, however, among the products of reduction of benzene-azo- $\beta$ -naphthyl acetate, obtained by us in accordance with the method previously described. Caustic soda does not dissolve any stable substance out of the mixed hydrochlorides, but simply gives a mixture of highly oxidisable bases, the chief constituent of which is undoubtedly  $\alpha$ -amido- $\beta$ -naphthol. The extreme reduction of the acetate therefore gives rise to the formation of aniline and  $\alpha$ -amido- $\beta$ -naphthol as chief products, a fact which is in itself of considerable importance in connection with the present line of investigation, since it shows that the acetyl-group is split off during reduction, and this lends support to the view that the said radicle is attached to oxygen, and not to nitrogen, in the original compound.

\* The formula proposed by one of the authors (Meldola, *Phil. Mag.*, Nov. 1888, p. 411) is for the present left out of consideration, because it indicates the formation of products of reduction identical with those indicated by No. I.

*Identification of  $\alpha$ -Amido- $\beta$ -Naphthol.*

At this stage of the work, seeing that the products of reduction of the acetyl-derivative contained some other base in addition to amido- $\beta$ -naphthol, it became necessary to discover a method by which the mixed bases could be converted into stable derivatives capable of being separated and characterised. The identification of the amido-naphthol itself presents but little difficulty, since it gives  $\beta$ -naphthaquinone on oxidation with ferric chloride. It is well known, however, that the formation of this quinone is somewhat capricious, and when formed it is not easy to identify, unless in a condition of tolerable purity. The quinone could not be obtained pure from our mixed hydrochlorides, because the oxidising agent also attacked the other base with which the amidonaphthol was mixed, and so gave rise to the formation of impurities of a resinous character. The method of oxidation being thus destructive to the other base, had to be abandoned. It was then found that the purified hydrochlorides when dissolved in water and treated in the cold with dilute hydrochloric acid and sodium nitrite, gave a crystalline, yellow substance which, after being collected and washed, was identified as nitroso- $\beta$ -naphthol (melting point about  $110^{\circ}$ ). This last substance is formed by the action of nitrous acid on  $\alpha$ -amido- $\beta$ -naphthol, according to a process of decomposition which has not hitherto been studied, but which has also been observed by Dr. H. E. Armstrong.\* The action of nitrous acid thus confirms the presence of  $\alpha$ -amido- $\beta$ -naphthol, but as this reagent did not appear to give a satisfactory product with the other base its use was also abandoned. Benzoyl and acetyl-derivatives of the mixed bases were next prepared, and these promised to answer our requirements, so that in the first place the benzoyl and acetyl-derivatives of pure  $\alpha$ -amido- $\beta$ -naphthol were prepared and studied, in order that we might familiarise ourselves with their properties. As these derivatives have not hitherto been described, we think it may be of use to give further particulars, as they are well characterised and stable crystalline substances, very easy of preparation, and thus offering many advantages over the quinone method for the identification of  $\alpha$ -amido- $\beta$ -naphthol, when the latter is mixed with other oxidisable bases.

Benzeneazo- $\beta$ -naphthol was reduced in alcoholic solution with tin and hydrochloric acid, the alcohol distilled off, and the amido-naphthol hydrochloride allowed to crystallise out of the solution in the usual way. This salt was collected, dissolved in water, and again crystallised with the addition of strong hydrochloric acid, this process

\* Private communication to one of the authors.

being repeated till the substance dissolved completely in water. The aniline and tin salts are thus got rid of, and the pure amidonaphthol hydrochloride is left as a white, crystalline compound. The latter was collected, drained completely from adhering mother-liquor, and dried in the water-oven. The dry salt was then just covered with glacial acetic acid, and powdered anhydrous sodium acetate and acetic anhydride added. The mixture was boiled for 2—3 hours, and the acetyl-derivative thrown out by dilution with water. The substance was collected, washed, and purified by crystallisation from alcohol, in which it readily dissolves when hot, and separates very slowly on cooling in the form of dense, colourless, transparent, rhombic prisms, melting sharply at 206°. Analysis showed that the compound was a diacetyl-derivative:—

0.1081 gram gave 0.2742 gram CO<sub>2</sub> and 0.0502 gram H<sub>2</sub>O.  
 0.1460 „ „ 7.6 c.c. moist N at 17° C. and 738.4 mm. bar.  
 0.3458 „ „ 18.2 „ „ 14.5° C. and 731.5 „

|         | Calculated for<br>$C_{10}H_6 \begin{smallmatrix} \text{NH} \cdot C_2H_5O \\ \text{O} \cdot C_2H_5O \end{smallmatrix}$ | Found. |      |
|---------|---|--------|------|
|         |   | I.     | II.  |
| C ..... | 69.13   | 69.18  | —    |
| H ..... | 5.35  | 5.16   | —    |
| N ..... | 5.76  | 5.84   | 5.94 |

The substance is accordingly acetamido- $\beta$ -naphthyl acetate. It is of interest to note that the acetylation in this case leads to the formation of a diacetyl-derivative and not of an anhydro-base, although the amidonaphthol is an ortho-derivative. As a parallel instance, we may mention  $\alpha$ - $\beta$ -naphthylenediamine which, although an ortho-compound, also gives a diacetyl-derivative, and not an anhydro-base, on acetylation (Lawson, *Inaug. Diss.*, 1885, p. 26).

By heating dry amido- $\beta$ -naphthol hydrochloride with anhydrous sodium benzoate and benzoyl chloride to the boiling point of the latter, for about two hours, a dibenzoyl-derivative is formed. The product of the reaction is washed repeatedly with hot water and dilute ammonia, and finally purified by two or three crystallisations from boiling alcohol, in which the substance dissolves somewhat sparingly. The pure compound forms whitish needles melting at 226.5°.

0.1186 gram gave 0.3420 gram CO<sub>2</sub> and 0.0544 gram H<sub>2</sub>O.  
 0.1508 gram burnt in a vacuum with CuO gave 5 c.c. moist N at 24.5° and 765.3 mm. bar.



|         |   |        |
|---------|---|--------|
|         | Calculated for  |        |
|         | $C_{10}H_6 \begin{cases} NH \cdot C_7H_5O \\ O \cdot C_7H_5O \end{cases}$ | Found. |
| C ..... | 78.47   | 78.66  |
| H ..... | 4.63  | 5.09   |
| N ..... | 3.81  | 3.73   |

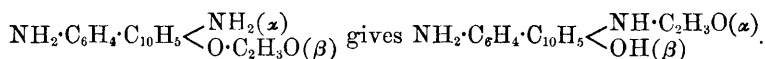
These results show that the compound is benzamido- $\beta$ -naphthyl benzoate and that, as in the case of acetylation, both the hydroxyl and amidogen of the amidonaphthol are simultaneously attacked.

*Mild Reduction of Benzeneazo- $\beta$ -Naphthol and its Acetyl-derivative.*

In accordance with the well-known fact that aromatic azo-compounds by mild reduction yield hydrazo-compounds, which under the influence of acids become transformed into bases of the diphenyl or naphthylphenyl series, it became of interest to investigate the action of mild reducing agents on the azo-compounds of  $\beta$ -naphthol. Commencing with the simplest case, benzeneazo- $\beta$ -naphthol was dissolved in a sufficient quantity of alcohol to retain the whole of the substance in solution when cold, and stannous chloride mixed with alcohol was added to the solution till reduction had been effected. The alcohol was distilled off, and the residual solution, after filtration to remove a small quantity of tarry matter, was mixed with dilute sulphuric acid, and allowed to stand for 24 hours. A small quantity of a crystalline substance, consisting of slender, white needles, had separated, but the yield was too small to enable analyses to be made. The presence of sulphuric acid was proved qualitatively in the compound after the latter had been purified by crystallisation from boiling water, in which it dissolves with great difficulty. The substance is in all probability the sulphate of diamido-oxynaphthylphenyl, and we hope to return to its investigation on a future occasion, but the small yield has deterred us from making further experiments in this direction, as the preparation of this compound has only an indirect bearing on the present line of work. The free base is very unstable, forming dark products of oxidation with extreme rapidity on exposure to the air. During the boiling of the solution of the sulphate for the purpose of purifying this salt, a considerable loss was incurred by the formation of a resinous product. If the sulphate is basified by ammonia, a greenish colouring matter is produced by the action of atmospheric oxygen. A small quantity of the sulphate heated with dry sodium acetate and acetic anhydride gave an acetyl-derivative, which, after crystallisation from alcohol, formed small, white needles melting at  $130-131^\circ$ .

Benzeneazo- $\beta$ -naphthyl acetate, when reduced in a similar manner

with stannous chloride in cold alcoholic solution, gives a mixture of bases from which nothing definite could be isolated. Amido- $\beta$ -naphthol is undoubtedly present, but not in sufficient quantity to separate out as a hydrochloride in the presence of excess of acid. The presence of amido- $\beta$ -naphthol was proved by the formation of nitroso- $\beta$ -naphthol by the action of sodium nitrite on the acid solution. The other base which is present is so readily decomposable that a dark resinous scum is continually formed during the evaporation of the solution. The addition of sulphuric acid to the solution of the hydrochlorides does not cause the separation of an insoluble sulphate. Nevertheless the absence of a naphthylphenyl base cannot be inferred from this circumstance, because it is highly probable that such a base, if formed, would contain the acetyl-group in one of the amidogens, and would thus lose the property of forming an insoluble sulphate. We have proved that such a naphthylphenyl-derivative is formed by a method which is described further on, so that the unstable base present in solution with the amidonaphthol is in all probability the acetyl-derivative of diamidohydroxynaphthylphenyl with the acetyl in one of the amidogen-groups by intramolecular transference, *i.e.*,

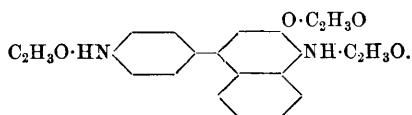


The proof that such a base is formed is furnished by the isolation of the diacetyl-derivative. The mixture of dry hydrochlorides, obtained by the reduction of benzeneazo- $\beta$ -naphthyl acetate in *slightly warm* alcoholic solution with stannous chloride, was boiled for about two hours with glacial acetic acid, dry sodium acetate, and acetic anhydride. The product was diluted with water, collected, washed, and crystallised two or three times from hot alcohol. Microscopic needles were obtained, melting sharply at 252°. From the first mother-liquor there slowly separated the familiar rhombic prisms of acetamido- $\beta$ -naphthyl acetate (m. p. 206°). The substance melting at 252° was analysed with the following results:—

|      |             |      |             |                 |     |             |                   |
|------|-------------|------|-------------|-----------------|-----|-------------|-------------------|
| I.   | 0.1513 gram | gave | 0.3892 gram | CO <sub>2</sub> | and | 0.0724 gram | H <sub>2</sub> O. |
| II.  | 0.1310      | „    | 0.3368      | „               |     |             |                   |
| III. | 0.1194      | „    | 0.3076      | „               | „   | 0.0581      | „                 |
| IV.  | 0.2154      | „    | 13.1 c.c.   | N at 15° C.     | and | 745 mm.     | bar.              |

|         | Calculated for<br>C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> . | Found. |       |       |      |
|---------|---|--------|-------|-------|------|
|         |   | I.     | II.   | III.  | IV.  |
| C ..... | 70.21   | 70.15  | 70.12 | 70.26 | —    |
| H ..... | 5.31  | 5.31   | —     | 5.40  | —    |
| N ..... | 7.44  | —      | —     | —     | 6.98 |

These numbers indicate that the compound is the triacetyl-derivative of diamido-hydroxynaphthylphenyl, the constitutional formula being—



The other base mixed with the amido- $\beta$ -naphthol is, accordingly, the monacetyl-derivative of diamido-hydroxynaphthylphenyl, the acetyl being most probably present in the  $\alpha$ -amidogen-group through intramolecular migration in the manner explained. The absence of two amidogen-groups in the monacetyl-derivative appears, as we have already stated, from the fact that it does not form an insoluble sulphate, a property which is so eminently characteristic of all the bases of the benzidine series, and which, as we have previously shown, pertains to diamido-hydroxynaphthylphenyl itself.

Summing up the results given by the present investigation of the products of reduction of benzeneazo- $\beta$ -naphthyl acetate, the following conclusions have been arrived at:—

1. By violent reduction with tin and hydrochloric acid, the chief product is  $\alpha$ -amido- $\beta$ -naphthol, a small quantity of the monacetyl-derivative of diamidohydroxynaphthylphenyl being at the same time produced. The splitting off of acetyl favours the view that this radicle is attached to the oxygen atom and not to the nitrogen atom.

2. Reduction in cold alcoholic solution with stannous chloride gives monacetyldiamido-hydroxynaphthylphenyl as the chief product,  $\alpha$ -amido- $\beta$ -naphthol being at the same time formed in smaller quantity.

3. Moderate reduction with stannous chloride in warm alcoholic solution gives a mixture of the two bases, from which the triacetyl-derivative of the hydroxynaphthylphenyl base can be isolated by acetylation and crystallisation of the product.

In all three cases, aniline is also one of the products of reduction.

#### *Reduction of Benzeneazo- $\beta$ -Naphthyl Benzoate.*

When this compound is reduced by boiling its alcoholic solution with tin and hydrochloric acid, the products are aniline and  $\alpha$ -amido- $\beta$ -naphthol, the benzoyl-group being split off as in the case of the acetate when it is submitted to violent reduction. A cold alcoholic solution of the benzoate, when mixed with a solution of stannous chloride, also gives a considerable quantity of amido- $\beta$ -naphthol together with a benzoyl-derivative of a naphthylphenyl base. The

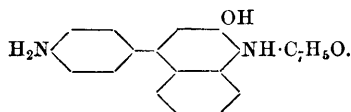
separation of the two products in this case offers no difficulty, as the basic properties of the latter are neutralised by the benzoyl-group and the substance is insoluble in dilute acids. After the reduction is complete, the alcohol is distilled off, the residue diluted with water and filtered. The filtrate contains the amido- $\beta$ -naphthol hydrochloride, which can be identified in the usual manner. The dark, tarry, insoluble residue left after this treatment is extracted two or three times with hot dilute hydrochloric acid, then washed with water, and finally extracted with cold alcohol, which dissolves out a tarry impurity and leaves the crude naphthylphenyl-derivative in the form of a whitish, crystalline powder. The latter, after being twice crystallised from boiling alcohol, in which it is rather sparingly soluble, forms white, silky needles melting at  $172-173^{\circ}$  :—

0.1004 gram gave 0.2860 gram  $\text{CO}_2$  and 0.0416 gram  $\text{H}_2\text{O}$ .

0.0813 gram burnt in a vacuum with  $\text{CuO}$  gave 5.5 c.c. moist N at  $14^{\circ}\text{C}$  and 750.9 mm. bar.

|         | Calculated for<br>$\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$ . | Found. |
|---------|--|--------|
| C ..... | 77.96  | 77.69  |
| H ..... | 5.08   | 4.60   |
| N ..... | 7.91   | 7.86   |

The formula deducible from these analyses indicates that the compound is a monobenzoyl-derivative of diamidohydroxynaphthylphenyl. The yield is not very great, as the chief products of reduction are, even under the described conditions of working, chiefly amido- $\beta$ -naphthol and aniline. The fact that the substance is not basic tells against the view that two amido-groups are present, and points to the transference of the benzoyl from the oxygen to the nitrogen in the naphthalene nucleus by the same process as that which takes place with the corresponding acetate. We are, therefore, led to the view that the constitutional formula of the compound is—



The proposed formula certainly indicates a phenolic substance, whereas our compound is insoluble in aqueous alkali. The disguising of the phenolic character of the molecule by the proximity of the  $\text{C}_7\text{H}_5\text{O}\cdot\text{NH}$ -group seems, however, more probable than that two free amido-groups should be present when the distinctly non-basic character of the substance is borne in mind. For this reason we attach the greater weight to the above formula.

The general conclusion to which these experiments point is that the acid radicle, acetyl or benzoyl, introduced into benzeneazo- $\beta$ -naphthol or its derivatives displaces an atom of hydrogen which is attached to oxygen and not to nitrogen. This is shown by the facility with which the radicle is split off during reduction and by the absence of acetanilide or benzanilide among the products of reduction. The transference of the radicle from the oxygen to the nitrogen in the naphthylphenyl base is effected by intramolecular change in the ortho-position, through the intermediate formation of an anhydro-base. An investigation of the products of reduction of the alkyl-derivatives of azo- $\beta$ -naphthol compounds has been carried on concurrently with the foregoing experiments, and the results will be made known in a subsequent communication. In the early part of the present research, we received much assistance from Mr. E. H. R. Salmon, and more recently we have had the benefit of the co-operation of Mr. J. H. Coste. It gives us much pleasure to acknowledge the services rendered by these gentlemen.

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