

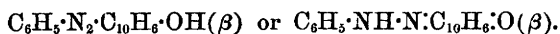
## LXIII.—Azo-Compounds of the Ortho-Series.

## Part I.

By RAPHAEL MELDOLA, F.R.S., and ERNEST M. HAWKINS.

*Preliminary.*

THE so-called oxyazo-compounds of the ortho-series represented by benzeneazo- $\beta$ -naphthol, the azo-derivatives of paracresol, &c., have already received a large share of attention from chemists on account of the interest attaching to the question of their constitution. The historical stages in the development of this question have frequently been recapitulated by one of the authors and his colleagues in former papers, and are now too well known to need repetition. The problem resolves itself into determining whether these compounds are hydrazones, or whether they are true azo-compounds, or whether both views can be entertained and the formulæ regarded as isodynamic (tautomeric). Thus, benzeneazo- $\beta$ -naphthol may, as is well known, be written



In spite of the numerous investigations which have been published, the question is still far from being settled, since the results point sometimes to the azo-formula and at others to the hydrazone formula. The two most recent investigations in connection with these compounds have led to contradictory conclusions, Noelting and Grandmougin deciding in favour of the azo-formula (*Ber.*, 1891, **24**, 1592), whilst Goldschmidt and Brubacher claim to have established the hydrazone formula (*ibid.*, 2300). If the formulæ are isodynamic, it would appear hopeless to decide the question by any chemical method, since whatever derivative may be examined it may be assumed that the one form is transformed into the other during the conversion. Thus the alkyl derivatives have the azo-formula (Meldola and Morgan, *Trans.*, 1889, **55**, 603), but it may be said that during alkylation the salt  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{OM}'$  is first formed by the transformation of the hydrazone, and that the alkyl group accordingly is attached to the oxygen. On this view it is difficult to see why benzeneazo- $\beta$ -naphthol is insoluble in aqueous alkalis unless we assume the existence of a closed ring of nitrogen and oxygen atoms (*Phil. Mag.*, Nov., 1888, 403; see also Meldola and Forster, *Trans.*, 1891, **59**, 710, note).

The products of reduction of the acetyl and benzoyl derivatives of benzeneazo- $\beta$ -naphthol were first investigated by one of the authors

and G. T. Morgan (Trans., 1889, **55**, 114). The results, as far as they went, appeared to support the azo-formula; that is, the acid radicle appeared to be attached to the oxygen. It is true that one of our arguments in favour of this conclusion was based upon negative evidence, but this evidence has recently become strengthened in an unexpected way, and it is therefore necessary to briefly call attention to these former results.

According to the view taken as to the constitution of benzeneazo- $\beta$ -naphthol, the acetyl derivative is either



A compound of the first formula, on reduction, would give aniline and amido- $\beta$ -naphthyl acetate, which, through the intermediate formation of an anhydro-base, would become transformed into acetamido- $\beta$ -naphthol (Böttcher, *Ber.*, 1883, **16**, 629 and 1933). A compound of the hydrazone (second) formula might be expected to give acetanilide and amido- $\beta$ -naphthol. By reduction with stannous chloride, we failed to obtain acetanilide or acetamido- $\beta$ -naphthol, the chief products being amido- $\beta$ -naphthol and a naphthylphenyl derivative.\* From the readiness with which the acetyl group was eliminated, it was concluded that this group was not attached to the nitrogen atom. This conclusion still appears to be unshaken, the stability of the grouping  $\text{C}_6\text{H}_5\cdot\text{N}(\text{C}_2\text{H}_3\text{O})$  being such as to make it improbable that cold reduction with stannous chloride would remove the acetyl.

After the publication of the foregoing conclusion, the reduction of the acetyl derivative of benzeneazo- $\beta$ -naphthol and of other ortho-oxyazo-compounds was repeated by Goldschmidt and Brubacher (*Ber.*, 1891, **24**, 2300) under different conditions and with results directly opposed to ours. These authors reduced with zinc dust and acetic acid in cold alcoholic solution, and obtained acetanilide and amido- $\beta$ -naphthol as the chief products, from which they quite justifiably decided in favour of the hydrazone formula. We repeated this experiment soon after the publication of the paper in the *Berichte*, and satisfied ourselves as to the correctness of their results, in so far as the formation of acetanilide was concerned. We were prepared to accept

\* The constitution of this base requires reinvestigation in view of the discovery recently announced simultaneously by Jacobson and W. Fischer (*Ber.*, 1892, **25**, 992), Witt and Schmidt (*ibid.*, 1013), and Täuber (*ibid.*, 1019). From the work of these authors, it appears that azo-derivatives of the *para*-series on mild reduction give rise to bases of the naphthylphenylamine and diphenylamine group and not of the naphthylphenyl or diphenyl group. Whether azo-derivatives of the *ortho*-series give similar products remains to be determined, and we propose to take up the question at the earliest opportunity (see also papers by Jacobson and others, *Ber.*, 1893, **26**, 681 *et seq.*).

the hydrazone formula, and attributed the discrepancy to the difference in the reducing agents employed (Trans., 1891, 59, 710). At the commencement of the present session we renewed our experiments with the object of throwing further light on the difference in the nature of the products of reduction obtained with different reducing agents. A preliminary experiment with the acetyl derivative of orthotolueneazo- $\beta$ -naphthol reduced with zinc-dust and acetic acid in cold alcoholic solution gave the unexpected result that acetamido- $\beta$ -naphthol was formed among the products of reduction. A similar result was obtained with the acetyl derivative of paratolueneazo- $\beta$ -naphthol. From the hydrazone formula, it is impossible to explain the formation of acetamido- $\beta$ -naphthol without making the assumption that acetyl is transferred from one nitrogen atom to the other. This is conceivable through the intermediate formation of a compound of the nature of an anhydro-base, as will be shown in our theoretical discussion of the results. At any rate, the formation of acetamido- $\beta$ -naphthol gave an entirely new aspect to the whole question and suggested an alternative explanation to that given by Goldschmidt and Brubacher. The experiments were accordingly extended to various azo-compounds of the ortho-series, and we have, in the first place, to submit the details of the work.

*Reduction of the Acetyl Derivative of Paratolueneazo- $\beta$ -Naphthol by Zinc-dust and Acetic acid.*

Paratolueneazo- $\beta$ -naphthol was first obtained by Zincke and Rathgen (Ber., 1886, 19, 2490). We found it advantageous in preparing this, and, in fact, all the azo-compounds employed in the present research, to use the method originally given by Liebermann for preparing benzeneazo- $\beta$ -naphthol (Ber., 1883, 16, 2859, note). The product, after crystallisation from alcohol, was acetylated by boiling for 24 hours with excess of acetic anhydride. The acetyl derivative fused to a dark red oil under boiling water, and was thus easily washed free from acetic anhydride. The compound was purified by crystallisation from alcohol and a specimen prepared for analysis by further crystallisation from benzene. When pure, it forms deep red prisms melting at 99°.

0.2032 gave 0.5576 CO<sub>2</sub> and 0.0997 H<sub>2</sub>O. C = 74.84; H = 5.45.

0.1746 „ 13.5 c.c. moist nitrogen at 10° and 758.6 mm. N = 9.23.

C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O requires C = 75.0; H = 5.25; N = 9.21 per cent.

The reduction was carried out as described by Goldschmidt and Brubacher, a cold saturated alcoholic solution being first prepared, then excess of zinc-dust added, and, finally, acetic acid, with constant

agitation till the reduction was complete. The reduction was conducted in a flask, the contents of which were kept cool during the process by immersion in cold water. The solution was filtered, and although nearly colourless at first, became orange in contact with the air, probably owing to the oxidation of a trace of hydrazo-compound. About one-half the alcohol was then distilled off, and the residue diluted with cold water, which caused the separation of a resinous-looking substance, which was collected, washed with water, and allowed to dry. We may at once dispose of this first product by stating that on further examination it turned out to be a mixture of some resinous product with acetoparatoluidide. That it also contained some hydrazo-compound was rendered probable from the circumstance that it became deep orange in the course of a few days' exposure to the air. The quantity of this product was very small as compared with the other compounds formed by the reduction, and in subsequent experiments it was altogether disregarded.

The filtrate from the first resinous precipitate was acidified with a little dilute hydrochloric acid to prevent the loss of basic compounds and evaporated in a dish on the water-bath till a crystalline scum began to appear. The dish was then allowed to cool for a day, by which time a considerable quantity of a crystalline substance had been deposited. The liquid was poured through a filter, the crystals washed with cold water and then extracted with cold dilute caustic soda. The alkaline solution was filtered, and, on acidifying with hydrochloric acid, silvery scales were gradually deposited. The crystalline substance thus obtained was collected, washed with water, and crystallised repeatedly from alcohol till the melting point was constant. We had not sufficient for analysis in this experiment, but the corresponding product from the reduction of the orthotolueneazo-compound had previously been analysed by us, and we were quite familiar with its appearance and properties. The solubility in cold alkali and the melting point of the pure compound, namely, 234—235°, left no doubt that we had in hand acetamido- $\beta$ -naphthol.\* The dry substance, heated in a tube, gave the peculiarly-smelling, oily anhydro-base, ethenyl- $\alpha$ -amido- $\beta$ -naphthol (Böttcher, *Ber.*, 1883, 16, 1939).

\* This compound furnishes another illustration of the fact, so frequently observed in the naphthalene series, that a trace of impurity too small to affect the results of analysis may nevertheless depress the melting point by many degrees. Thus Böttcher first assigned the melting point 225°. In our notes we had entered the melting point as 227°. Grandmougin and Michel then gave it as 230° (*Ber.*, 1892, 984), which they subsequently corrected to 235° (*ibid.*, 3433). Many crystallisations from alcohol are necessary to bring the melting point up to this last temperature.

The portion of the crystalline deposit insoluble in cold alkali was crystallised two or three times from boiling water, finally with the addition of animal charcoal, and was thus obtained in the form of large, white needles melting at  $147^{\circ}$ , and having all the properties of acetoparatoluidide.

0.1680 gave 13.4 c.c. moist nitrogen at  $12^{\circ}$  and 764.6 mm.  $N = 9.51$ .  
 $C_7H_7 \cdot NH \cdot C_2H_5O$  requires  $N = 9.39$  per cent.

The filtrate from the crystalline deposit, which consists, as we have shown, of a mixture of acetoparatoluidide and acetamido- $\beta$ -naphthol, was evaporated to a small bulk and divided into two portions. One was tested for amido- $\beta$ -naphthol by means of sodium nitrite and hydrochloric acid. Only a trace of a yellow substance was deposited on long standing, and this was too small to identify as  $\beta$ -naphthoquinone. We do not infer from this, however, that no amido- $\beta$ -naphthol is formed by the reduction. It may safely be asserted, for reasons which will appear subsequently, that it is among the products, but, being present only in small quantity, is lost by oxidation during the evaporation. The other portion of the filtrate was treated with excess of caustic potash till the precipitate of zinc hydroxide at first formed was redissolved. The alkaline solution, which smelt strongly ammoniacal, was shaken up with benzene in a separating funnel, the benzene solution separated, washed two or three times with water, and then with dilute hydrochloric acid. The acid liquor was drawn off, evaporated to a small bulk, made alkaline with caustic potash, and then extracted with ether. The ethereal extract on evaporation left a very small quantity of an oily base which solidified on standing and had all the properties of paratoluidine. It was identified by Rosenstiehl's test (strong sulphuric and nitric acids).

The reduction described in this experiment was performed with about 20 grams of the acetyl derivative. Acetoparatoluidide appears to be the chief product; acetamido- $\beta$ -naphthol, ammonia, paratoluidine, and (probably) amido- $\beta$ -naphthol are formed in much smaller quantities.

Although perhaps superfluous, we thought it advisable to satisfy ourselves that acetamido- $\beta$ -naphthol was not formed during the process of acetylation. A quantity of the acetyl derivative of paratolueneazo- $\beta$ -naphthol similar to that which was reduced in the previous experiment was finely powdered and extracted with cold caustic soda. The filtrate on acidifying gave no trace of acetamido- $\beta$ -naphthol. The latter compound is undoubtedly a true product of the reduction.

*Reduction of the Acetyl Derivative of Paratolueneazo- $\beta$ -naphthol with Zinc-dust and Formic acid.*

In order to make certain that the acetic acid used in the previous experiment took no part in the formation of the acetamido- $\beta$ -naphthol found, a fresh portion of the purified acetyl derivative was reduced as before, substituting formic for acetic acid. After reduction and filtration, the alcohol was nearly all distilled off, the solution diluted with water, and after the addition of a little dilute hydrochloric acid, evaporated to the crystallising point. The crop of crystals which separated, after standing for some hours, was dealt with as in the previous experiment. Cold dilute caustic acid dissolved out a substance which was precipitated by acids, and which, after repeated crystallisation from alcohol, had a melting point of  $234-235^{\circ}$ , and was identified as acetamido- $\beta$ -naphthol. The portion insoluble in alkali was crystallised several times from boiling water using animal charcoal, and, as before, proved to be acetoparatoluidide; m. p.  $147^{\circ}$ .

0.1758 gave 14.5 c.c. moist nitrogen at  $13^{\circ}$  and 753.6 mm.  $N = 9.66$ .

$C_7H_7 \cdot NH \cdot C_2H_5O$  requires  $N = 9.39$  per cent.

The liquor drained from the crystalline deposit was divided into two portions, one of which was examined for amido- $\beta$ -naphthol by the nitrite test. On standing for some time, a trace of  $\beta$ -naphthaquinone separated from the solution. The remainder of the filtrate was made alkaline with excess of caustic potash, when ammonia was again evolved, extracted with benzene, the benzene solution extracted with dilute hydrochloric acid, and the acid liquid made alkaline with caustic soda. Paratoluidine was present in sufficient quantity to separate from the solution on standing. It was collected, purified by redissolving in dilute acid, filtering the solution, and reprecipitating by alkali. The purified product had the odour, crystalline appearance, and melting point ( $45^{\circ}$ ) of paratoluidine. It was further identified by Rosenstiehl's test. The products of reduction in this case also are, therefore, acetoparatoluidide, acetamido- $\beta$ -naphthol, amido- $\beta$ -naphthol, paratoluidine, and a trace of ammonia.

This experiment was made roughly quantitative in order to get some idea of the relative quantities of the acetoparatoluidide and acetamido- $\beta$ -naphthol. The other products could not very well be determined.

Acetyl derivative taken .....	19.0 grams.
Crude acetoparatoluidide, that is, portion <i>insoluble</i> in alkali and containing resinous impurities .....	7.8 ,,
Crude acetamido- $\beta$ -naphthol, that is, portion <i>soluble</i> in alkali .....	0.3 ,,

*Reduction of the Acetyl Derivative of Orthotolueneazo- $\beta$ -naphthol with Zinc-dust and Acetic acid.*

The azo-compound was prepared and acetylated in the same manner as the paratolueneazo- $\beta$ -naphthol employed in the previous experiments. After two or three crystallisations from alcohol, the acetyl derivative (about 15 grams) was reduced in cold alcoholic solution with zinc-dust and acetic acid in precisely the same way as before. The alcoholic filtrate containing the products of reduction was largely diluted with water, and a small quantity of a resinous precipitate removed by filtration.\* The alcohol was then distilled off, and the residual liquor evaporated as before to the crystallising point. Owing to the greater solubility of acetorthotoluidide in water, the evaporation had to be carried further, and acetamido- $\beta$ -naphthol began to separate first. The whole crystalline deposit was extracted with alkali in the usual manner, and the solution acidified with hydrochloric acid. Sufficient acetamido- $\beta$ -naphthol was obtained in this experiment for analysis. The crude compound, after repeated crystallisation from alcohol, had the right melting point, 235°.

0.2378 gave 0.6251 CO<sub>2</sub> and 0.1228 H<sub>2</sub>O. C = 71.69; H = 5.74.  
 0.1519 „ 1.23 c.c. moist nitrogen at 15.5° and 761.9 mm. N = 7.05.  
 C<sub>10</sub>H<sub>6</sub>(OH)·NH·C<sub>2</sub>H<sub>3</sub>O requires C = 71.64; H = 5.47; N = 6.96 p. c.

The portion of the crystalline deposit insoluble in alkali was crystallised several times from hot water, with the addition of powdered animal charcoal. The pure compound was identified by its melting point as acetorthotoluidide, 107°, and this was confirmed by analysis.

0.1960 gave 0.5194 CO<sub>2</sub> and 0.1277 H<sub>2</sub>O. C = 72.27; H = 7.24.  
 0.1526 „ 12.3 c.c. moist nitrogen at 9° and 751.5 mm. N = 9.55.  
 C<sub>7</sub>H<sub>7</sub>·NH·C<sub>2</sub>H<sub>3</sub>O requires C = 72.48; H = 7.38; N = 9.39 per cent.

The products contained in the residual liquor in this experiment were not further investigated, as the amido- $\beta$ -naphthol appeared to have been lost by oxidation during the evaporation, and the previous experiments with the corresponding *para*-compound had given all the necessary information as to the nature of these products. The *simultaneous* formation of acetorthotoluidide and acetamido- $\beta$ -naphthol

\* This product, which is of no immediate importance, is only formed in very small quantity. It was not crystallisable from any solvent. A specimen was dissolved in glacial acetic acid, the filtered solution diluted with water, and the whitish, flocculent precipitate collected, washed, and dried. On combustion, it was found to contain 4.45 p. c. N, a quantity not agreeing with that required by the hydrazo-compound or any other product which might be expected to result from the reduction.



is the point of chief importance in connection with the interpretation of the results.

## Part II.

By R. MELDOLA and F. B. BURLS.

### *Further Experiments on the Reduction of the Acetyl Derivative of Benzeneazo- $\beta$ -naphthol.*

As already stated in the preliminary considerations, a repetition of Goldschmidt and Brubacher's reduction of this compound with zinc-dust and acetic acid led us to the same conclusion as these authors. The products of the reduction were acetanilide, aniline, and amido- $\beta$ -naphthol. But although we detected no acetamido- $\beta$ -naphthol at the time of making the experiment, subsequent experience has shown that a small quantity of this compound mixed with a large quantity of acetanilide is very easily overlooked, and we did not consider it as finally established that acetamido- $\beta$ -naphthol was absent. The formation of aniline rendered it probable that this compound might be found among the products of reduction on more careful examination. Further experiments were therefore undertaken with the following results.

*Reduction with Zinc-dust and Hydrochloric acid.*—Excess of zinc-dust was added to a cold saturated solution of the acetyl derivative in alcohol, and then dilute hydrochloric acid drop by drop with constant agitation. The reduction in this case was very tardy, and had to be completed by adding a few drops of strong hydrochloric acid towards the end of the operation. After filtration, the alcohol was distilled off, the liquor diluted with water, filtered to remove a resinous product, of which a small quantity was thrown out on dilution, and then evaporated on the water-bath till a crystalline scum began to make its appearance. After standing for a day, a considerable deposit of white, crystalline scales had separated. The deposit was collected, washed with water, and extracted in the cold with dilute caustic soda, in which the greater part of the crystals dissolved. On adding acid to the alkaline filtrate, a reddish precipitate was obtained which did not consist chiefly of acetamido- $\beta$ -naphthol, as in the former reduction experiments, but contained a small quantity of this compound mixed with some substance which was uncrystallisable, and which was not further examined. The only conclusion that could be drawn concerning the nature of this resinous product was that it consisted of or contained some compound of the nature of a hydrazo-compound, since it gradually became reddened by oxidation on exposure to the air. The product precipitated from the



alkaline solution by acid was purified by dissolving in alcohol, and fractionally precipitating with water. The resinous substance above referred to was by this means first removed, and the filtrate on further dilution gave a deposit of crude acetamido- $\beta$ -naphthol. The latter was purified by repeated crystallisation from alcohol, and identified by its melting point and other properties.

The portion of the crystalline deposit left undissolved by alkali was dissolved in a little glacial acetic acid, the solution diluted with water, and then agitated with ether. The latter solvent, on being separated and allowed to evaporate, gave a trace of a substance which crystallised from boiling water in the characteristic scales of acetanilide, with which it was identified by its melting point ( $114^{\circ}$ ).

The filtrate from the crystalline deposit was found to contain large quantities of amido- $\beta$ -naphthol and aniline.

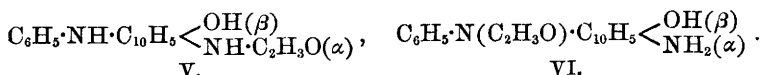
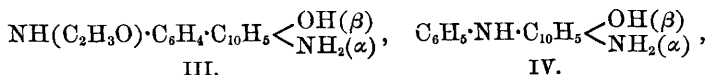
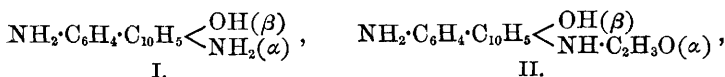
The results obtained in this experiment appear to be of considerable importance, since acetamido- $\beta$ -naphthol is undoubtedly produced, although only in small quantities. Still less acetanilide appears to be formed by this method of reduction. Although about 20 grams of the acetyl derivative were used in the experiment, we did not obtain sufficient of either of these compounds for analysis. The chief products are amido- $\beta$ -naphthol and aniline, from which it appears that the acetyl group is very readily removed by the reducing agents employed.

*Reduction with Zinc-dust and Acetic acid.*—This was in every respect a repetition of the previous experiment, acetic acid being substituted for hydrochloric acid. About 25 grams of the acetyl derivative were reduced, and the crystalline product left after evaporation was extracted in the usual way with dilute caustic soda. A small quantity of acetamido- $\beta$ -naphthol was found in the alkaline filtrate by the usual method, and was identified by its melting point, &c., after several crystallisations from alcohol. The other products were not examined, as we had already satisfied ourselves that these were, as stated by Goldschmidt and Brubacher, acetanilide, amido- $\beta$ -naphthol, and aniline. The formation of acetamido- $\beta$ -naphthol has, however, been overlooked by these investigators, as it was also by us in our earlier experiments. It required considerable experience and familiarity with the properties of this compound before we were enabled to isolate and identify it when in admixture with a large quantity of acetanilide and other products. As it is formed only in small quantity by the method of reduction adopted by Goldschmidt and Brubacher, it is not at all surprising that it should have escaped detection by these authors.\*

\* According to their method of separation, in which the acetanilide is extracted by ether, the acetamido- $\beta$ -naphthol would be found in the residual aqueous liquor.

*Reduction by Stannous Chloride in the Cold.*—This was a repetition of former work (Meldola and Morgan, Trans., 1889, 122) undertaken with the special object of ascertaining whether acetanilide and acetamido- $\beta$ -naphthol could be detected among the products of reduction with all the experience gained by the preceding experiments. In order to make the conditions as favourable as possible for the retention of the acetyl group, the reduction was effected in the cold and an excess of hydrochloric acid was avoided. The following method was found to work most successfully:—

The acetyl derivative of benzenazo- $\beta$ -naphthol, purified by crystallisation from alcohol, was placed in a flask and just covered with a saturated solution of stannous chloride prepared by dissolving the crystalline salt in water and allowing it to remain for many days in contact with an excess of tin. An equal bulk of alcohol was added, and the flask, fitted with a cork, was allowed to stand in cold water for several days, the contents being agitated from time to time. More stannous chloride and alcohol were added occasionally till the crystalline acetyl derivative had all passed into solution, and an almost colourless liquor had been obtained. The alcohol was then distilled off, the residual liquor largely diluted with water and allowed to stand. After some hours, a copious white precipitate had separated. This was collected, washed into a separating funnel, and well agitated with ether. The ethereal extract, on evaporation, left only a very small trace of a crystalline substance decomposing with blackening at about  $160^{\circ}$ , and therefore not consisting of acetanilide. The filtrate from the white precipitate was similarly extracted with ether, but no acetanilide was found in the extract. This filtrate, on further examination, was found to contain small quantities of aniline and amido- $\beta$ -naphthol. The white precipitate was dissolved in hot water, filtered, and the resinous residue specially examined for acetamido- $\beta$ -naphthol, but none could be found. The white precipitate consisted almost entirely of the supposed naphthylphenyl base referred to in the paper alluded to above. It forms the chief product in this method of reduction, and in the light of recent researches may have the constitution expressed by any one of the six formulæ\*



\* I and IV on the assumption that acetyl is eliminated.

The further investigation of this base will be made the subject of a separate study which has already been commenced, since the clearing up of its constitution may throw light on the position of the acetyl group, and thus on the constitution of the acetyl derivative of benzeneazo- $\beta$ -naphthol. The results herein recorded are, so far, completely confirmatory of the conclusions arrived at in 1889. With stannous chloride under the most favourable conditions, no acetanilide or acetamido- $\beta$ -naphthol is produced. In so far as reduction is complete—and this occurs only to a very small extent—the products are amido- $\beta$ -naphthol and aniline; the chief product is the naphthylphenyl or naphthylphenylamine base. The latter can be easily prepared in large quantities by the method described.

*Reduction of the Acetyl Derivative of Parachlorobenzeneazo- $\beta$ -naphthol by Zinc-dust and Acetic acid.*

The original azo-compound was described by one of us and F. W. Streatfeild in a former paper (Trans., 1888, 53, 676). For the present purpose, it was prepared in the usual way from parachloraniline hydrochloride,  $\beta$ -naphthol (emulsified), and sodium nitrite. After purification, the product was acetylated by boiling for 24 hours with acetic anhydride. The acetyl derivative is readily soluble in alcohol, whereas the original compound is but slightly soluble in this solvent. The pure compound forms magnificent, flat needles crystallising in large bundles, and having a deep red colour. The melting point is 133°.

0.1415 gave 10.8 c.c. moist nitrogen at 13.3° and 741.8 mm. N = 8.77.  
0.1990 „ 0.0878 AgCl. Cl = 10.94.

$C_{18}H_{13}N_2O_2Cl$  requires N = 8.62; Cl = 10.93 per cent.

In this experiment our object was to ascertain whether an acid substituent, such as chlorine, increased or diminished the quantity of acetamido- $\beta$ -naphthol formed on reduction. The method of reduction was the same as that followed in the previous experiments and need not be redescribed. The crop of crystals obtained on evaporation was treated with dilute caustic soda and filtered. From the alkaline filtrate, only a very small quantity of precipitate was obtained on acidifying, and after several crystallisations from alcohol, a trace of acetamido- $\beta$ -naphthol was obtained, just sufficient for identification by its melting point. The crystalline residue insoluble in alkali was crystallised once or twice from dilute acetic acid and finally from dilute alcohol. It consisted of long, white needles melting at 176°, and proved to be acetoparachloranilide.\*

\* The melting point of this compound is given by Beilstein and Kurbatow as 172.5° (Annalen, 182, 98). Goldschmidt and Pollak give 171° (Ber., 1892, 1328).

0.3545 gave 0.2988 gram AgCl. Cl = 20.87.

0.1306 „ 9.45 c.c. moist nitrogen at 16.5° and 764 mm. N = 8.45.

$C_6H_4Cl \cdot NH \cdot C_2H_5O$  requires Cl = 20.94; N = 8.26 per cent.

The filtrate from the crystalline deposit was divided into two portions, one of which was found, by the nitrite test, to contain amido- $\beta$ -naphthol, and the other, on being made alkaline by caustic soda, yielded a base which was readily extracted by ether, and which by its melting point (70°) and other properties was identified as parachloraniline.

It appeared from this experiment that the presence of an acid substituent in the benzene nucleus tends rather to diminish the quantity of acetamido- $\beta$ -naphthol formed. Our next efforts were therefore directed towards an azo-compound containing a greater number of positive radicles in the benzene nucleus.

*Reduction of the Acetyl Derivative of Pseudocumeneazo- $\beta$ -naphthol by Zinc-dust and Acetic acid.*

The azo-compound, which does not appear to have been described, was prepared in the usual way, and purified by successive crystallisations from glacial acetic acid and benzene. The compound is but very slightly soluble in boiling alcohol, and from this solvent it separates slowly in the form of dense prismatic needles having a bronzy-green metallic lustre. From benzene and glacial acetic acid, in which it is much more freely soluble, it separates in fine needles of a brilliant scarlet colour. It dissolves in strong sulphuric acid with a magenta-red colour which remains unchanged on dilution.

The pure compound melts at 163–164°.

0.1040 gave 0.3003  $CO_2$  and 0.0578  $H_2O$ . C = 78.75; H = 6.17.

0.1693 „ 13.8 c.c. moist nitrogen at 14° and 770.6 mm. N = 9.72.

$C_9H_{11}N_2 \cdot C_{10}H_6 \cdot OH$  requires C = 78.62; H = 6.20; N = 9.65 per cent.

The acetylation of this compound presented difficulties, as after 24 hours boiling with acetic anhydride, the product was found to be a mixture of the acetyl derivative with unaltered substance. We have not been able to isolate the acetyl derivative in a state of purity,\* but the experiments have not been extended very far in this direction, because, for our present work, the crude mixture answered all requirements. The product of acetylation was washed with water, dissolved in alcohol, and the solution filtered to remove the unaltered

\* The acetylation would probably have been more complete if we had added anhydrous sodium acetate, as in the original method employed by one of us and F. J. East, Trans., 1888, 53, 466.

azo-compound as far as possible. The crystals deposited from the alcoholic filtrate were dried, dissolved in benzene, and the solution allowed to deposit four successive crops of crystals. The melting points were :—

I, 150—151°; II, 114—116°; III, 77—85°; IV, 75—77°.

The first crop was rejected, and the others mixed together and used for reduction. 5 grams were dissolved in alcohol, and reduction effected with zinc-dust and acetic acid in the usual way. After the excess of alcohol had been distilled off, the contents of the flask were transferred, without loss, to a porcelain dish, diluted with water and a little hydrochloric acid, and allowed to stand. A crystalline pulp was thus obtained, which was collected, washed with water, and extracted with cold dilute caustic soda, as in the previous experiments. The alkaline filtrate contained a considerable quantity of acetamido- $\beta$ -naphthol, which was thrown out by acid, collected, washed, and dried. The portion insoluble in alkali consisted of acetocumidide mixed with resinous impurities. The actual quantities obtained were

Acetyl derivative (crude) taken .....	5.0	grams.
Portion insoluble in alkali, and consisting of crude acetocumidide .....	1.57	„
Portion soluble in alkali, and consisting of crude acetamido- $\beta$ -naphthol .....	0.46	„

The acetamido- $\beta$ -naphthol was purified by repeated crystallisation from alcohol, and identified by its melting point. The acetocumidide was purified by crystallisation from boiling water, dilute acetic acid, and dilute alcohol successively, and obtained finally in the form of long, white needles melting at 163°.

0.1228 gave 0.3339 CO<sub>2</sub> and 0.0946 H<sub>2</sub>O. C = 74.19; H = 8.55.  
0.1034 „ 7.1 c.c. moist nitrogen at 13° and 759.7 mm. N = 8.09.  
C<sub>9</sub>H<sub>11</sub>·NH·C<sub>2</sub>H<sub>3</sub>O requires C = 74.57; H = 8.47; N = 7.91 per cent.

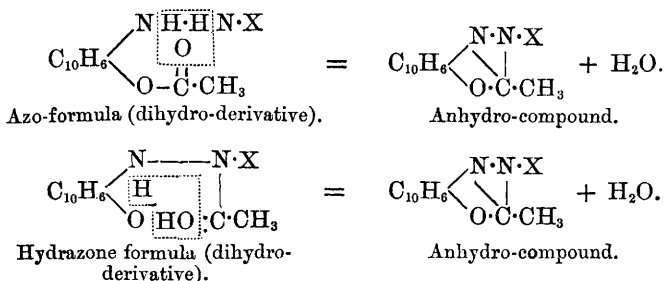
The acid filtrate from the total crystalline deposit was found to contain amido- $\beta$ -naphthol and a considerable quantity of pseudocumidide (m. p. 63°) when treated as in the previous experiments.

The results now described show that the yield of acetamido- $\beta$ -naphthol obtained on reduction is much increased when the diazotised base combined with the  $\beta$ -naphthol contains several methyl groups. Thus the acetyl derivative of tolueneazo- $\beta$ -naphthol yields more than the acetyl derivative of benzeneazo- $\beta$ -naphthol, and the acetyl derivative of pseudocumeneazo- $\beta$ -naphthol more than the corresponding tolueneazo-compound. There can be no doubt that this

compound is one of the normal products of reduction of acetylated azo- $\beta$ -naphthol,\* and no theory of the constitution of these compounds can be regarded as satisfactory which leaves the formation of acetamido- $\beta$ -naphthol unaccounted for.

*Bearing of the Results on the Theory of the Constitution of the  
Orthoazo-compounds.*

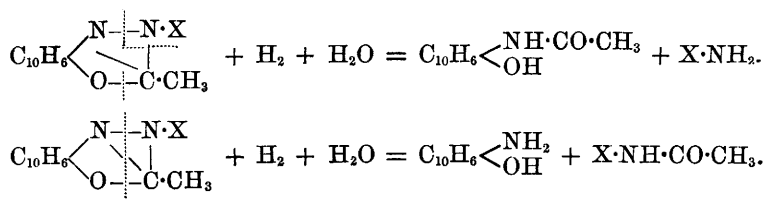
If the formation of acetanilide, acetotoluidide, acetocumidide, &c., is regarded as evidence in favour of the hydrazone formula, the formation of acetamido- $\beta$ -naphthol must be considered as evidence against this formula and in favour of the "azo-" constitution. Unless the acetyl derivatives of the azo-naphthols are mixtures (or molecular compounds) of both forms, for which there is no evidence, the results now obtained are apparently contradictory and irreconcilable with either azo- or hydrazone formula. The discrepancy disappears, however, if we assume that an unstable intermediate compound of the nature of an anhydro-base is formed during the reduction. The first product of the reduction of an azo-compound is probably in all cases a hydrazo-compound (Meldola and Forster, *Trans.*, 1891, **59**, 711). By the elimination of hydrogen with the oxygen of the acetyl group in the form of water, such a condensation product would be formed. But this leaves the question of the original position of the acetyl group still unsolved, as it will be seen from the following formulæ that the same anhydro-compound would result, whether the acetyl were attached originally to the oxygen or the nitrogen atom :—



We have no direct evidence of the formation of this intermediate compound; it may occur among the resinous bye-products of reduction, but, as stated in this paper, no definite crystallisable compound

\* According to the quantitative experiments, the acetyl derivative of paratoluenazo- $\beta$ -naphthol gives about 1.6 per cent., and the corresponding pseudocumeneazo-compound about 9.2 per cent. of acetamido- $\beta$ -naphthol on reduction.

could be isolated from these bye-products. The "anhydro-" compound may, however, be incapable of existence in the free state, being but an unstable intermediate phase of the reduction.\* Such an intermediate stage is undoubtedly passed through during the reduction of the acetyl derivatives of orthonitrophenols, the acetyl group being by this means transferred from the oxygen to the nitrogen atom (Böttcher, *Ber.*, 1883, **16**, 629 and 1933). The assumption of an intermediate compound is therefore warranted not only by analogy with the orthonitrophenols, *but such an assumption alone enables us to explain the formation of acetanilide as well as acetamido-β-naphthol and the other products of reduction.* This is shown by the following schematic formulæ:—



Both modes of decomposition appear to take place simultaneously, separation, accompanied by reduction and hydrolysis, occurring as indicated by the dotted lines. The amount of each kind of decomposition is determined by the nature of the radicle X.

The results now made known appear to us to destroy the value of the evidence in favour of the hydrazone formula based by Goldschmidt and Brubacher on the formation of acetanilide from the acetyl derivatives of the orthoazo-compounds on reduction. At the same time, our results do not disprove this formula; they leave the question in precisely the same state as before. Much more work will be necessary before the problem can be solved. Experiments with other orthoazo-compounds and with alkoyl radicles other than acetyl are in progress, and the results will be communicated in due course. We may point out that the solution of this problem is not without interest in connection with the general question of the constitution of organic colouring matters, since the acetyl derivatives of the orthoazo-compounds are all highly-coloured substances.

We desire, in concluding, to acknowledge the assistance which we received towards the end of the investigation from Mr. F. Southerden.

*Finsbury Technical College.*

\* Goldschmidt and Brubacher have also suggested the possibility of such an intermediate product being formed, but they reject it as "höchst unwahrscheinlich" (*Ber.*, 1891, 2303).