XXXV.—*Orientation Effects in the Diphenyl Series. Part V. The Independence of the Two Nuclei in Diphenyl Compounds.*

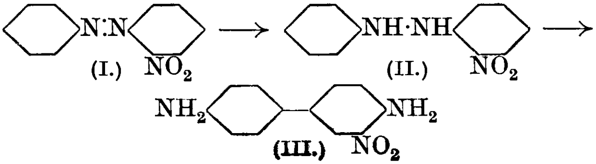
By Raymond James Wood Le Fèvre and Eustace Ebenezer Turner.

The Nitration of Phthalylbenzidine and the Preparation of 3-Nitrobenzidine.

On a previous occasion (J., 1926, 2041) we stated that 2-nitrobenzidine, m. p. 143°, is obtained on hydrolysing the product of nitrating phthalylbenzidine in excess of concentrated sulphuric acid. Koller, on the other hand, isolated as the sole product a red, crystalline solid, m. p. 192°, which he regarded as 3-nitrobenzidine (*Ber.*, 1904, **37**, 2880). In view of Koller's very definite statements, we have re-investigated the above nitration and also prepared 3-nitrobenzidine by a process which established its constitution. Precise repetition of Koller's nitration has led to excellent yields of 2-nitrobenzidine, together with a small quantity of a mixture of substances melting at 185—195° which is not separable into its components, and corresponds in these and other respects to a mixture of 2-nitro- and 2 : 3′-dinitro-benzidine.

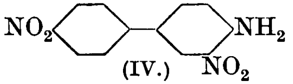
The preparation of 3-nitrobenzidine has presented many difficulties. We first attempted to obtain it by nitrating a number of *NN′*-disubstituted benzidines. The mononitration of diacetylbenzidine has already been shown (*loc. cit.*) to be impracticable owing to the insolubility of this substance in any nitrating mixture which does not effect dinitration. We now find that benzidine condenses rapidly with most esters at the boiling point of the latter, and in this way 4 : 4′-*diethyloxamidodiphenyl*, $(CO_2Et{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot})_2$, and similar compounds have been prepared. This compound and *NN′*-dicarbethoxybenzidine, $(CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot})_2$, are considerably more soluble than diacetylbenzidine, yet neither compound could be caused to undergo mononitration only. Dinitration is readily effected, and that of the oxamido-derivative affords what is up to the present the most convenient method of preparing Strakosch's dinitrobenzidine.

A second synthesis of 3-nitrobenzidine was attempted by the process (I) ⟶ (II) ⟶ (III) :



Bamberger and Hübner (*Ber.*, 1903, **36**, 3803) found that 2-nitroazobenzene was converted by alkali sulphides into 2-phenylbenztriazole 1-oxide, but Green and Bearder (J., 1911, **99**, 1960) effected the reduction of 2 : 2′-dinitroazobenzene to the corresponding hydrazo-compound. On submitting 2-nitroazobenzene to Green and Bearder's reduction conditions, however, we obtained the triazole oxide as the sole product.

The preparation of 3-nitrobenzidine was finally accomplished by reducing 3 : 4′-dinitro-4-aminodiphenyl (IV) with hot aqueous-alcoholic ammonium sulphide, this method being suggested by the known stability of *o*-nitroaniline towards this reagent. 3-*Nitrobenzidine* is almost insoluble in alcohol, from which solvent Koller claimed to have crystallised it. It melts at least 15° higher than Koller's product. Its diacetyl derivative, clearly the first stage in the formation of Strakosch's dinitrobenzidine from diacetylbenzidine, affords 3 : 3′-dinitrodiacetylbenzidine on nitration. Moreover, 3-nitrobenzidine depresses the m. p. of the product, m. p. 185—195°, obtained by us from phthalylbenzidine, so that it is probable that little if any 3-nitrobenzidine is formed in the latter process. The absence of appreciable amounts of the 3-nitro-compound suggests that nitration occurs in nucleus B (V) rather than in (A).



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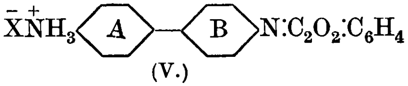
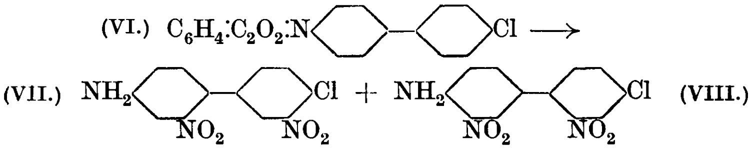


(V.)

Mononitration of 4-*chloro*-4′-*phthalimidodiphenyl* (VI) could not be effected, and dinitration, followed by hydrolysis, gave a mixture of (VII) and (VIII). It is probable that 4-chloro-2′-nitro-4′-phthalimidodiphenyl and 4-chloro-2-nitro-4′-phthalimidodiphenyl are respectively the precursors of (VII) and (VIII) (compare the nitration of 4 : 4′-dihalogenodiphenyls; Dennett and Turner, J., 1926, 476). 4-*Bromo*-4′-*phthalimidodiphenyl* also has been found to undergo 2 : 3′- and 2′ : 3-nitration.



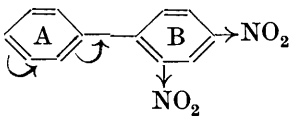
The Independence of the Two Nuclei.

Superficial consideration of the known orienting effects in the diphenyl series suggests that a group present in one nucleus (say B in IX) has a direct influence on the position or positions taken up by a second group entering the other nucleus (A). We do not, however, think this is the case, and prefer to regard the first substituent as producing its effect indirectly, that is, merely by modifying the orienting properties of nucleus B. The modified B nucleus remains ortho-para directing whatever the nature of the first substituent, and a group then entering nucleus A invariably takes up the 4′- (to a lesser extent the 2′-) position. When the 4′-position is occupied by an ortho-para directing group, the modified B nucleus frequently appears to exert quite a small ortho-para influence.

Were a direct orienting effect transmitted from a group present in nucleus B to substitutable positions in A, 2- and 4-nitrodiphenyl would be expected to undergo at any rate a certain amount of 3′-nitration, since the source of electron drift will be the 4′-carbon atom (IX). Since 3′-nitration does not occur, it is clear that in this sense A and B are independent. Similarly, from the work of Burton and Kenner (J., 1922, **121**, 489) and from some experiments we have made, it seems probable that nitro-groups present in one nucleus cannot effect the activation of halogen atoms or nitro-groups present in the other nucleus.* Both sets of facts agree with the conception of A and B as two independent mobile *cyclo*hexatrienoid systems connected in the 1 : 1′-positions by an invariable single bond, which is not a link in a true conjugated system.

The nitration of 2- or 4-nitrodiphenyl may be compared with that of ω-nitrostyrene. Here there is no mobile conjugation (electronic tautomerism) between the side chain and the nucleus, and therefore the effect of the nitro-group cannot be transmitted to the nucleus to any extent. Again, therefore, meta-nitration does not occur.

The assumption of mobility of conjugation throughout the naphthalene molecule appears to explain the nitration of α-nitronaphthalene in positions 5, 8, and 3 (compare Pictet, *Compt. rend.*, 1893, **116**, 815) (formulæ X and XI). There are doubtless factors other than a simple electron drift regulating substitution in naphthalene compounds, but we think it worth while to point out the



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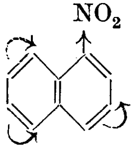
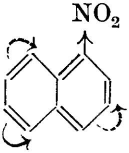


(X.)



(XI.)

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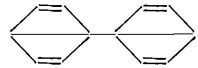
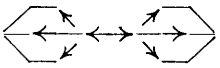
* After this paper had been written, the authors noticed that Robinson and Zaki (J., 1927, 2485) had arrived at very similar conclusions from a different point of view.

contrast between naphthalene and diphenyl. It is likely that a halogen atom or a nitro-group present in position 5 or 7 in naphthalene would be rendered reactive if nitro-groups were present in positions 1 and 3.

The discussion of the independence of the two benzene nuclei in diphenyl derivatives leads us to a recent paper by Bell and Kenyon (J., 1926, 3044). These authors criticise adversely a formula (XII) suggested by one of us (*Nature*, 1923, **112**, 439) at a time when, as we now know, the very facts of diphenyl chemistry were untrustworthy. It is clear that recent work in the diphenyl series does not necessitate formula (XII), except in such a modernised form as (XIII), which, however, is by no means unsatisfactory as a basis for explaining the laws of substitution in the diphenyl series. We must, however, differ with Bell and Kenyon in the interpretation of their experimental results. They found that 4-hydroxydiphenyl coupled with benzenediazonium chloride in position 3, and reacted with chloroform in the presence of alkali to give what they regarded, we think rightly, as the 3-aldehyde. They stated that formula (XII) " demands " 4′-reaction in both cases. Yet few will dissent from the view that the orienting effect of the charged oxygen atom decreases with distance, and it is curious that Bell and Kenyon should have overlooked the fact that on the basis of formula (XII) the 4′-position is not less than three times as distant as the 3- and 5-positions, which (compare the 3- and 5-positions in *p*-cresol) are in any case *competing for the reagent.* Nor is it certain that the two reactions chosen do not depend on the possibility of keto-enol tautomerism, which would be clearly impossible between the 4- and 4′-positions in 4-hydroxydiphenyl, but probable between the 3- and 4-positions.

(XII.)





(XIII.)

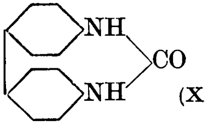
Had these authors used a 3 : 5-disubstituted hydroxydiphenyl, their results might have borne their interpretation. We find that 3 : 5-dibromo-4-hydroxydiphenyl, a substance prepared by Bell and Kenyon (*loc. cit.*), does not couple at any measurable rate with diazotised sulphanilic acid, a reagent used because of its known advantages as compared with diazotised aniline.

We have not investigated the Reimer–Tiemann reaction with the dibromo-compound, because so little is known of the mechanism of this reaction, which is neither unidirectional nor quantitative. Our experiment, however, settles the point raised, *i.e.*, it shows that the charged oxygen atom present (in alkaline solution) in 4-hydroxydiphenyl does not confer reactivity on the 4′-position.

The Condensation of Benzidine with Carbamide.

Schiff and Vanni (*Annalen*, 1890, **258**, 363), by heating " benzidinediurethane " with benzidine, obtained a substance which they regarded as (XIV) identical with a compound previously obtained by Schiff (*Ber.*, 1878, **11**, 830) by heating benzidine with carbamide. In neither of these papers, however, were any analyses quoted. Michler and Zimmermann, apparently unaware of the results of Schiff (1878, *loc. cit.*), prepared " carbonylbenzidine " by the interaction of carbonyl chloride and benzidine, and considered this compound also to have formula (XIV) (*Ber.*, 1881, **14**, 2178).

Snape (*Chem. News*, 1896, **73**, 37), by treating diphenyl-4 : 4′-dicarbimide, $NCO\cdot C_6H_4\cdot C_6H_4\cdot NCO$, with ammonia, obtained a compound which was in turn stated, on very slight evidence, to be identical with Schiff's compound. From its mode of formation, it is almost certainly (XV).



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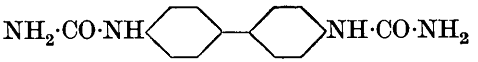


(XV.)

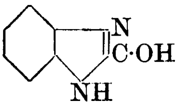
The present authors have shown (J., 1926, 2476) that the "carbonylbenzidine " of Michler and Zimmermann is certainly not (XIV) but is either $(NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH)_2CO$ or a substance of more complex structure, *e.g.*, as produced by the reaction :

$$EtO_2C\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CO_2Et + 2NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2 = 2EtOH + (NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot)_2.$$

We have prepared Schiff's benzidine-carbamide compound and regard it as identical with Snape's compound and not with the unknown carbonylbenzidine (XIV) nor with the " carbonylbenzidine " of Michler and Zimmermann, for on subliming, the latter compound does not decompose, whereas the condensation product of benzidine and carbamide does. Moreover, one molecule of benzidine always reacts with two molecules of carbamide when the two substances are heated together in various proportions. Conclusive evidence cannot be obtained owing to the chemical and physical properties of the substances concerned.

In view of the present position of the Kaufler formula, analogies will no longer be expected between pairs of substances such as benzidine and *o*-phenylenediamine. These two bases behave quite differently towards carbamide. The former, according to the evidence given above, reacts with carbamide as does aniline, with the formation of the analogue of phenylcarbamide, $NH_2\cdot CO\cdot NHPh$, whereas the latter is converted into 2-hydroxybenziminazole (XVI) (Kym, *J. pr. Chem.*, 1907, **75**, 323), the analogue of the hypothetical carbonylbenzidine (XIV). Moreover, as Hartmann showed (*Ber.*, 1890, **23**, 1047), *o*-phenylenediamine hydrochloride is converted by carbonyl chloride into the above benziminazole, but by potassium cyanate into an entirely different substance, " *o*-phenylene diureide " (XVII) (Lellmann, *Ber.*, 1883, **16**, 598). A close analogy has been repeatedly observed between 1 : 2-disubstituted benzene derivatives and 2 : 2'-disubstituted diphenyl compounds. In the present case, the analogy holds, for 2 : 2'-diaminodiphenyl is converted by carbamide into a true carbonyldiaminodiphenyl (XVIII) (Niementowski, *Ber.*, 1901, **34**, 3325).

The condensation product of benzidine and carbamide, *i.e.*, *NN'*-dicarbamylbenzidine, dissolves in concentrated sulphuric acid to give a solution which is coloured an intense reddish-purple by traces of nitrates. One gram of potassium nitrate could thus be detected in 500,000 c.c. of concentrated sulphuric acid. At greater dilutions, the test failed; diphenylamine, however, still gave a coloration after the addition of water. The new reagent is unaffected by nitrites when present at about the same concentrations as the nitrates.



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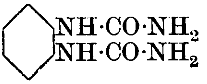

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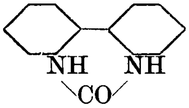

(XVIII.)

EXPERIMENTAL.

Nitration of Phthalylbenzidine.—Phthalylbenzidine (50 g.) previously crystallised from nitrobenzene (compare Kuhn, Jacob, and Furter, *Annalen*, 1927, **455**, 254) was nitrated in sulphuric acid at — 10° according to the directions of Koller (*loc. cit.*). After $\frac{1}{4}$ hour, the solution was poured on ice, and the brown, gelatinous precipitate obtained was filtered off and washed by suspension in hot water, steaming, and filtration while hot. The cooled yellow filtrate, on being basified with ammonia, gave a bright red substance (A) (1·2 g.), m. p. 156—160°.

A solution of the residual paste in 250—300 c.c. of concentrated sulphuric acid was heated at 130° for 30 minutes, cooled, and diluted with much water, 7 g. of a dark reddish powder (B) being obtained. The filtrate, when partly basified, gave a light yellow powder (C) (20 g.), m. p. above 225°. The filtrate from this, on complete basification, gave a red, gummy solid which, after being steamed, changed to a red, crystalline suspension (D) (11 g.), m. p. 140—141°. The m. p. of this product was not lowered by admixture with 2-nitrobenzidine.

Fraction A was extracted with alcohol, leaving a sparingly soluble yellow powder. The extract deposited an indefinite red powder, m. p. about 175°. Further crystallisation did not affect the m. p. of this product, which was, however, clearly a mixture. The mother-liquors from these crystallisations were precipitated with water, giving a bright red powder (0·5 g.), m. p. 191—195° with previous shrinking. A mixture of this product with 3-nitrobenzidine melted indefinitely at 185—190°.

B and C contained unhydrolysed phthalyl compounds. Hydrolysis was effected with alcoholic-aqueous potassium hydroxide at a temperature not exceeding 40°, and the solution was somewhat diluted and filtered (Filtrate E). The residue (dark red, 11 g.) was freed from inorganic matter (5·7 g.) by extraction with boiling alcohol. Evaporation of the extract gave 4 g. of red crystals, m. p. 128—130°. These were combined with 5 g. of similarly melting material obtained by the complete dilution of E and the whole was crystallised from hot 70% sulphuric acid. A cream-coloured paste of the 4 : 4′-disulphate was obtained, and this changed into the yellow 4-sulphate on addition of water. Complete neutralisation of the yellow sulphate gave 5·5 g. of a deep red solid, m. p. 134—137°. Mixed with 2-nitrobenzidine, this melted at 136—137°. Extraction with much alcohol left a residue (0·7 g.), m. p. 190—200°, which, after being crystallised from phenol–alcohol, had m. p. 210—215°.

The total yield of 2-nitrobenzidine is estimated as 20 g. (theoretical yield, for mononitration, 27 g.; but some dinitration clearly occurred).

Condensation of Esters with Benzidine.—The following substances of high m. p. were obtained by gently boiling a solution of benzidine in excess of the appropriate ester under reflux for the times stated, and were isolated by addition of alcohol, filtration, and extraction with boiling alcohol.

NN′-*Di*-o-*carbethoxybenzoylbenzidine.*—After ¾ hour, the ethyl phthalate solution deposited small, yellow plates. These melted above 300° and were insoluble in all common solvents (Found: N, 5·6. $C_{32}H_{24}O_6N_2$ requires N, 5·3%).

4 : 4′-*Diethyloxamidodiphenyl.*—After ¼ hour (ethyl oxalate being used), a sudden deposition of pearly plates occurred. These were very slightly soluble in hot glacial acetic acid and crystallised from this solvent in plates (Found: N, 7·5. $C_{26}H_{20}O_6N_2$ requires N, 7·3%).

NN′-*Dicinnamoylbenzidine.*—After 30 minutes (ethyl cinnamate being used), yellow crystals appeared, but heating was continued for another hour. The final product was a yellow, crystalline powder, insoluble in ordinary solvents (Found : N, 6·7. $C_{30}H_{24}O_2N_2$ requires N, 6·3%).

NN′-*Dicarbethoxybenzidine.*—The following method was found preferable to that given by Schiff and Vanni (*loc. cit.*). Well-powdered benzidine (30 g.) was treated slowly with 30 g. (almost 2 mols.) of ethyl chloroformate, the flask being warmed gently during the process, and kept well shaken. The pasty mass gradually became a loose powder. About 20 c.c. of alcohol were added, followed later by warm dilute hydrochloric acid. The liquid was filtered, and the extraction with acid repeated until the filtrate no longer set to a stiff gel on cooling. The residue was crystallised from 270 c.c. of boiling glacial acetic acid. Dilution of the acetic acid mother-liquor also gave stiff gels.

3 : 3′-*Dinitrobenzidine.*—4 : 4′-Diethyloxamidodiphenyl (5 g.) was slowly dissolved in a mixture of 35 c.c. of nitric acid (*d* 1·5) and 25 c.c. of glacial acetic acid, the temperature being kept below 25°. After 5 minutes, the reddish solution was gradually diluted; needles separated, and these crystallised from 200 c.c. of glacial acetic acid in yellow needles, m. p. 216—217° (Found : N, 11·7. $C_{20}H_{18}O_{10}N_4$ requires N, 11·8%). Hydrolysis with 60—70% sulphuric acid gave a crude base, m. p. 273—274°.

Attempts to effect mononitration of the oxamido-derivative led either to unchanged material or to impure dinitro-compound.

Dinitration of NN′-*Dicarbethoxybenzidine.*—This compound (2 g.), dissolved in 50 c.c. of glacial acetic acid, was treated with 1·5 g. of nitric acid (*d* 1·5) dissolved in 5 c.c. of glacial acetic acid. After 1 hour's heating at 90—100°, separation of yellow crystals (2 g.) was complete. The 3 : 3′-dinitro-compound so obtained crystallised from rectified spirit in plates, m. p. 216—217° (Found : N, 13·6. $C_{18}H_{20}O_8N_4$ requires N, 13·3%).

2-*Nitro*-NN′-*dicarbethoxybenzidine.*—The reaction between 2-nitrobenzidine (5 g.) and ethyl chloroformate (10 g.) began spontaneously and was completed by heating for 10 minutes at 90—100° in presence of 20 c.c. of rectified spirit. The product (6 g.) after treatment with water crystallised from rectified spirit in orange, irregular, spear-shaped plates, m. p. 187—188° (Found : N, 10·9. $C_{18}H_{21}O_6N_3$ requires N, 11·0%).

2 : 2′-*Dinitro*-NN′-*dicarbethoxybenzidine.*—This compound was readily formed, but less readily than the preceding one (heating for 1 hour). It formed a microcrystalline, yellow powder, m. p. 200—201° (Found : N, 13·7. Calc. : N, 13·3%).

2 : 3′- *and* 3 : 3′-*Dinitro*-NN′-*dicarbethoxybenzidines.*—The appropriate dinitrobenzidines did not react with ethyl chloroformate

under the above conditions. In each case, therefore, 1·5 g. of dinitro-base were heated with 2 c.c. of the ester, heating being continued for 2 hours at 120°, and for 6 hours at 140°, in the case of the 2 : 3′- and the 3 : 3′-compound, respectively.

2 : 3′-*Dinitro*-NN′-*dicarbethoxybenzidine* formed bunches of needles, m. p. 158°, from hot dilute acetic acid (Found : N, 13·5%).

3 : 3′-*Dinitro*-NN′-*dicarbethoxybenzidine* formed yellow crystals from acetic acid; m. p. 216—217° (not depressed by the addition of the product of dinitrating the parent urethane).

4-*Chloro*-4′-*nitrodiphenyl*.—4-Nitrodiphenyl containing a little stannic iodide was chlorinated at a temperature just above its m. p. After the calculated increase in weight had occurred, the product became a pasty mass on cooling. It was stirred with alcohol, and the almost colourless solid was then crystallised from glacial acetic acid. It formed pale yellow needles, m. p. 157—158°, and was identified as follows. Nitration at the ordinary temperature with nitric acid (*d* 1·5) gave a product which, after being crystallised from glacial acetic acid, melted at 153—154°. This reacted with piperidine to give 2 : 3′ : 4-trinitro-4′-piperidinodiphenyl (Le Fèvre and Turner, J., 1926, 2041).

3-*Nitrobenzidine*.—4-Acetamidodiphenyl (111 g.) was obtained by acetylating the crude product from the reduction of 160 g. of 4-nitrodiphenyl, iron powder, water, and ferric chloride being used. The acetamido-compound was found to nitrate better by the following method than by that mentioned by Scarborough and Waters (J., 1927, 1133).

The acetamido-compound (21 g.) was slowly added to a mixture of 200 c.c. of nitric acid (*d* 1·5) and 100 c.c. of glacial acetic acid, the temperature being kept below 20°. After 5 minutes, the solution was poured into water, and the precipitate was crystallised from much acetic acid.

The dinitro-compound so obtained was hydrolysed by dissolving it in concentrated sulphuric acid, adding water until separation of solid occurred, and then heating at 125° for ½ hour. The solution was then diluted and filtered, and the whole of the crude base reduced as follows :

A suspension of base (25 g.) in 250 c.c. of rectified spirit and 250 c.c. of concentrated aqueous ammonia was boiled under reflux, and a current of hydrogen sulphide passed through it. Aqueous ammonia was added from time to time. After 1 to 1·5 hours, all the suspended solid dissolved, and was replaced by a red, crystalline precipitate. This was filtered off and crystallised from alcohol (yield, 13 g.). Its m. p., 208—210°, was not affected by further crystallisation (Found : N, 19·5. $C_{12}H_{11}O_2N_3$ requires N, 18·3%).

3-*Nitrobenzidine* forms very characteristic, chocolate-brown leaflets with a coppery reflex, and is almost insoluble in alcohol.

The *diacetyl* derivative was prepared by adding 8 c.c. of acetic anhydride to a boiling solution of 2 g. of the base in 40 c.c. of glacial acetic acid. After ½ hour, water was added until precipitation began. On cooling slowly, yellow needles separated, m. p. 249—250°. The diacetyl derivative was added to nitric acid (*d* 1·5) at 0°, the solution added to excess of water, and the product hydrolysed in the usual manner. The base obtained was identical with 3 : 3′-dinitrobenzidine.

4-*Chloro- and* 4-*Bromo*-4′-*phthalimidodiphenyl*.—These were obtained by heating with phthalic anhydride (160—170° ; 2 hours) the crude products resulting from the iron–water–ferric chloride reduction of 4-chloro- and 4-bromo-4′-nitrodiphenyl, respectively. The *chloro*- and the *bromo*-derivative both form pale yellow needles from *cyclo*hexanol and melt at 245° and 260°, respectively.

Nitration of 4-*Chloro*-4′-*phthalimidodiphenyl*.—To a suspension of 18 g. of the chloro-compound in 100 c.c. of nitric acid (*d* 1·4) were added 150 c.c. of nitric acid (*d* 1·5), the temperature being maintained below 15°. The solution was poured into water, and the precipitate collected and dried. It was dissolved in a mixture of 150 c.c. of concentrated sulphuric acid and 10 c.c. of water, and the solution was heated at 130—140° for 10 minutes and then gradually diluted. The resulting crude base (18 g.) was treated with 400 c.c. of boiling alcohol. The undissolved portion (7·5 g.) had m. p. 190—200°, and after crystallisation from glacial acetic acid, m. p. 213°. This product was identical with 4-chloro-2 : 3′-dinitro-4′-aminodiphenyl (Le Fèvre and Turner, *loc. cit.*). The filtrate from the 7·5 g. of residue yielded a product which could not be purified by crystallisation, but was converted into 2 : 3′-dinitrobenzidine when it was heated at 160—180° in a sealed tube for 7 hours with alcoholic ammonia. Thus, 18 g. of chlorophthalimido-compound gave 7 g. of 4-chloro-2 : 3′-dinitro-4′-aminodiphenyl and 5 g. of 2 : 3′-dinitrobenzidine (after crystallisation from phenol–alcohol).

Nitration of 4-*Bromo*-4′-*phthalimidodiphenyl*.—Nitration was carried out in the manner described for the chloro-compound. From the mixed crude hydrolysis product, only 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl was obtained after replacement of the amino-groups by bromine atoms (perbromide method).

Preparation of NN′-*Dicarbamylbenzidine*.—No details for the preparation are given in the literature; *e.g.*, Schiff (*loc. cit.*) merely " heated carbamide with benzidine."

When benzidine (1 mol.) was heated at 140—145° in three different experiments with 1, 2, and 3 mols. of carbamide, respectively, until ammonia was no longer evolved, and the cooled products were exhaustively extracted with boiling alcohol, the three condensations gave 41, 85, and 85%, respectively, of the theoretically obtainable quantity of dicarbamylbenzidine.

The preparation of this substance is most conveniently carried out by rapidly evaporating an alcoholic solution containing benzidine (1 mol.) and carbamide (2 mols.), transferring the finely divided, intimate mixture so obtained into a number of boiling tubes, and heating these in a bath kept at 140—145°. Evolution of ammonia at once occurs, and when it has ceased, the resulting hard grey masses are extracted with alcohol as before. The dicarbamylbenzidine so obtained, after being dried at 120°, forms a light grey or almost white powder, insoluble in all common solvents, and not melting below 300°.

The dicarbamyl compound is also readily obtainable by slowly treating a solution of 5·1 g. of benzidine hydrochloride in 300 c.c. of water with one of 1·7 g. of potassium cyanate in 100 c.c. of water. After 4 hours, the precipitate is collected, and purified as described above.

Colour reactions with nitrous and with nitric acid. Two 0·02% solutions in concentrated sulphuric acid were prepared: (A) Dicarbamylbenzidine, and (B) potassium nitrate. Measured volumes of B were diluted with 10, 20, 30, etc., volumes of concentrated sulphuric acid. One c.c. of A was added to 10 c.c. of diluted solutions of B. One c.c. of B diluted by 100, 150, and 200 c.c. of sulphuric acid, respectively, gave a rich port-wine colour, a pale reddish-purple colour, and a very faint pink colour, respectively. Addition to the most dilute solution of a few drops of stock diphenylamine solution (in dilute sulphuric acid) caused the development of a marked blue colour. From these results it is seen that dicarbamylbenzidine will detect 1 g. of potassium nitrate with certainty in the presence of 500,000 c.c. of sulphuric acid. If large volumes are used, the colour is visible at 1·5 times this dilution.

A solution of sodium nitrite (0·005 g.) in 25 c.c. of concentrated sulphuric acid was treated with 1 c.c. of A. No coloration was produced. When 0·1 c.c. of B was added, a bluish-purple colour at once developed.

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