

Action of Acid Anhydrides on Benzidine.

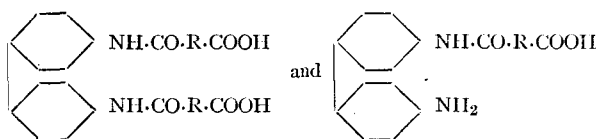
By

Akira Shimomura.

(Received September 2, 1924)

ABSTRACT.

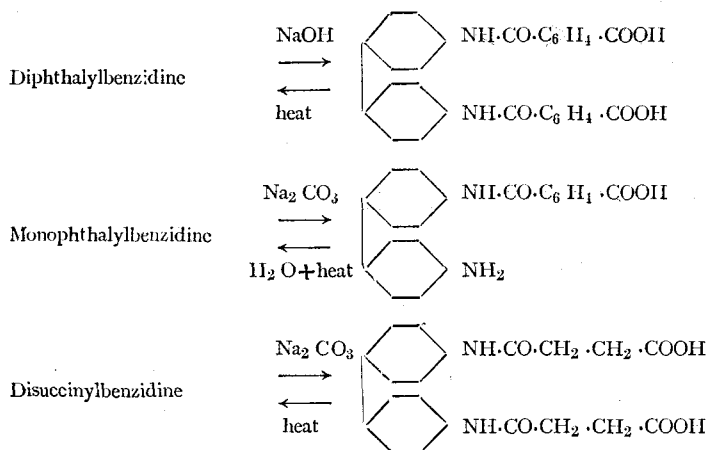
Some anhydrides of dicarboxylic acids were found to form with benzidine in alcohol or benzene solution at the ordinary or a little higher temperature, addition products of the general formulae



Phthalic anhydride, succinic anhydride and diphenic anhydride gave addition products of the above type, while naphthalic anhydride did not.

The mechanism of formation of mono- and di-phthalylbenzidine is discussed from the results obtained by the reaction between benzidine and phthalic anhydride.

The following reactions were found reversible:

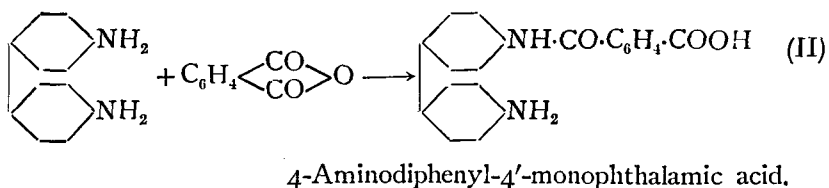
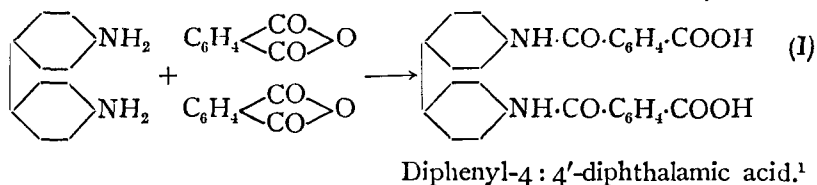


The possibility of a novel formula for diphthalybenzidine is suggested as the result of transformation of monophthalybenzidine to diphthalybenzidine by the action of another molecule of phthalic anhydride.

The preparation and properties of diphenyl-4:4'-diphthalamic acid, 4-aminodiphenyl-4'-monophthalamic acid, diphenyl-4:4'-disuccinamic acid, disuccinylbenzidine, dinaphthalybenzidine, diphenyl-4:4'-diphenamic acid and 4-aminodiphenyl-4'-monodiphenamic acid are described.

In the course of work on certain derivatives of diphthalybenzidine, certain reactions were observed which could not be cleared up without further investigation. This led to a review of the work done in reference to acyl derivatives of benzidine, and by working under conditions different from those employed by others, the following results were obtained.

Diphthalybenzidine (Bandrowski, Ber., 1884, 17, 1182) is prepared by heating phthalic anhydride and the base at 200° for several hours. The reaction carried out in solution at the ordinary or a little higher temperature, however, was found different from that in a dry state, giving rise to addition products of the following constitution:



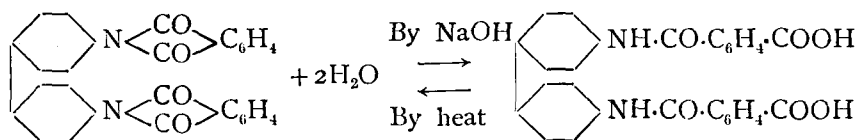
The excess of phthalic anhydride and the use of an anhydrous solvent such as benzene seem to give chiefly the di-addition product (I), while the use of a hydrated solvent like dilute alcohol helps the formation of (II). The separation of (I) and (II) was accomplished by

¹ This compound was first prepared by Cain and Brady T., 101, 2306, (1912.) by heating the mixture of benzidine (1 mol.) and phthalic anhydride (2 mols.) moistened with nitrobenzene at 100° for one hour.

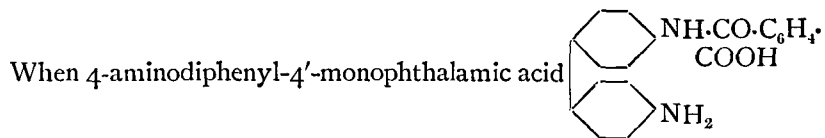
passing carbon dioxide into the alkaline solution of the mixture, whereby the less acidic (II) was first precipitated while the dicarboxylic acid (I) was kept in solution.

When the colourless (I) was heated at above 100° (say $130-140^{\circ}$) for several hours, it lost two molecules of water, turning into diphthalylbenzidine which is yellow.

Diphthalylbenzidine, on the other hand, was easily converted into diphthalyl-4 : 4'-diphthamic acid (I) by the action of sodium hydroxide. Hence the following reaction is reversible :

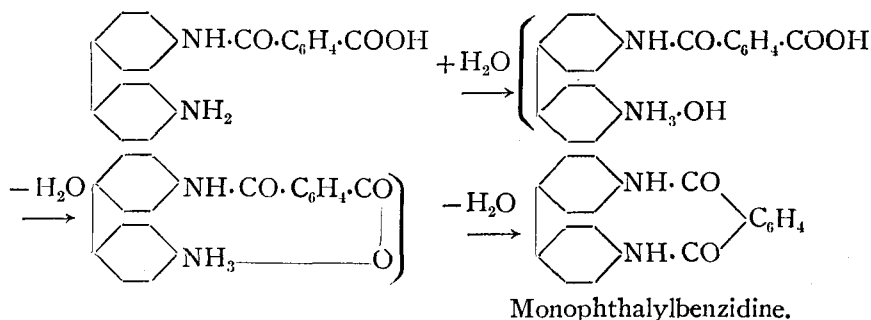


Monophthalylbenzidine, prepared according to Koller (Ber., 1904, 37, 2882) by boiling the mixture of phthalic anhydride and benzidine in aqueous suspension, behaved somewhat differently towards alkalis from the diphthalyl-compound, *i. e.*, it was mostly decomposed into phthalic acid and benzidine by the action of sodium hydroxide on heating, while the corresponding mono-carboxylic acid (II) was obtained by a milder treatment with sodium carbonate, which had almost no action in the case of diphthalylbenzidine.



was precipitated from the alkaline solution, in which it was easily soluble, by means of mineral or acetic acid, it was thrown down invariably in combination with more or less of the added acid, which could not be removed by mere washing. The precipitation of the free amino-acid, however, was effected by passing carbon dioxide into the alkaline solution.

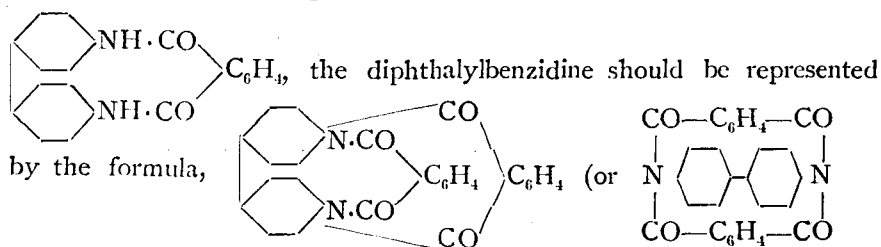
This compound did not give monophthalylbenzidine on heating, but darkened and melted towards $291-300^{\circ}$ with decomposition. On boiling with water for several hours, it was converted into a yellow powder, which was found to be monophthalylbenzidine. Judging from the results of the above experiments, the following scheme is suggested :



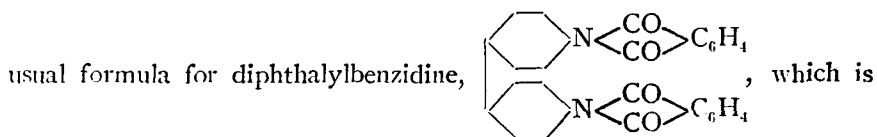
The above investigation seems to give an insight into the mechanism of reactions involved in the usual processes of making mono- and diphtalylbenzidines. When benzidine and phthalic anhydride are fused together, we may suppose that at first the addition product is formed which by further heating loses water and is converted into diphtalylbenzidine.

In the case of monophthalybenzidine, the corresponding addition product is also probably formed, which in the presence of water and on heating is subsequently transformed into monophthalybenzidine.

When monophthalybenzidine was heated with another molecule of phthalic anhydride at 200° , diphtalylbenzidine was obtained. Although this experiment looks very simple, it raises an interesting point in regard to the constitution of diphenyl. If Kaufler's stereo-formula (Ann., 1907, 351, 151; Ber., 1907, 40, 3250) is accepted and the monophthalybenzidine represented by the formula

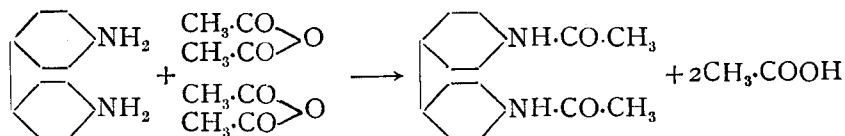


according to the usual formula of diphenyl), unless we assume that there has been such a change of constitution in monophthalybenzidine during heating that one NH_2 -group has been left free, in order to give the



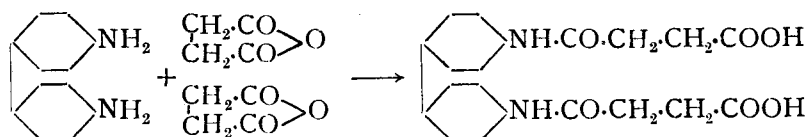
not a very probable assumption.

In the case of the anhydride of a mono-basic acid such as acetic anhydride, there is no possibility of formation of a carboxylic acid of the type (I), for the resulting substance would probably be diacet, 1-benzidine. It may be pointed out that the reaction is similar to the previous one, the addition taking place, with the splitting off of one molecule of acetic acid from one molecule of acetic anhydride.



This occurred both in alcoholic and benzene solutions when benzidine and acetic anhydride were combined at the ordinary temperature.

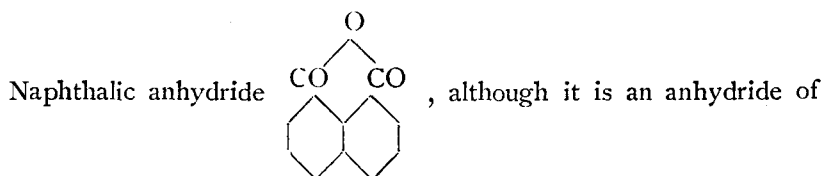
With succinic anhydride, on the other hand, a similar reaction to that of phthalic anhydride was found to take place both in alcoholic and benzene solutions.



Diphenyl-4 : 4'-disuccinamic acid.

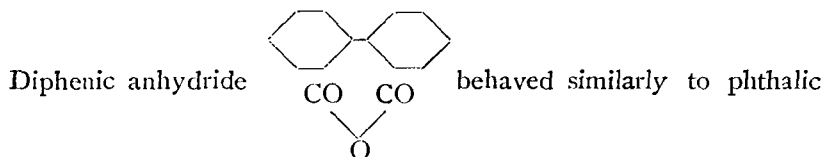
The conversion of the dicarboxylic acid into disuccinylbenzidine by elimination of two molecules of water was accomplished with much greater difficulty than with diphtalamic acid. The same difference was also observed in preparing disuccinylbenzidine by fusion, a much higher temperature being needed to bring about combination of the benzidine and succinic anhydride. At lower temperatures, the addition product, *i.e.*, diphenyl-4 : 4'-disuccinamic acid was found to be the main product.

Disuccinylbenzidine was only partly converted into diphenyl-4 : 4'-disuccinamic acid by prolonged heating with dilute soda solution, while with caustic alkali, it was mostly decomposed into its components.



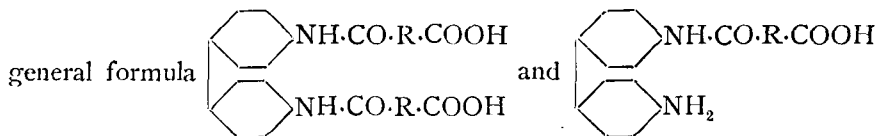
a dibasic acid, did not react with benzidine in alcoholic, benzene or xylene solution, even at the boiling temperature, to form the usual

addition product. Dinaphthalylbenzidine (probably with some mononaphthalyl derivative), on the other hand, was prepared by heating 1 mol. of benzidine and 2 mols. of naphthalic anhydride at about 200° for four hours, and the product was found extremely stable towards the hydrolysing action of acid and alkali.



and succinic anhydrides as regards formation of the addition product, *i.e.*, diphenyl-4:4'-di-diphenamic acid (probably with some 4-aminodiphenyl-4'-mono-diphenamic acid).

It is interesting to note that, in general, the mode of reaction between benzidine and an acid anhydride depends largely on the nature of the anhydride and the solvent used. In some cases, the reaction does not take place at all, and even when the addition product of the



are formed, their respective properties often differ widely. (For details, see experimental part).

I might add that all these high-melting addition and condensation products present analytical difficulties, for most of them burn explosively the moment the combustion starts.

EXPERIMENTAL.

Action of Acetic Anhydride on Benzidine in Solution.

In alcoholic solution.— An alcoholic solution of benzidine, containing 0.92 gm. (1 mol.) of the base in 30 c.c. of alcohol, was added at 15° to an alcoholic solution of acetic anhydride, containing 1.02 gm. (2 mols.) of the anhydride in 10 c.c. of the solvent. On shaking, diacetylbenzidine appeared soon as a colourless crystalline precipitate with evolution of a little heat. After having been left at the room temperature for a few days, the product was filtered, washed with warm alcohol and dried. The yield was 1.1 gram and the product did not melt below 300°.

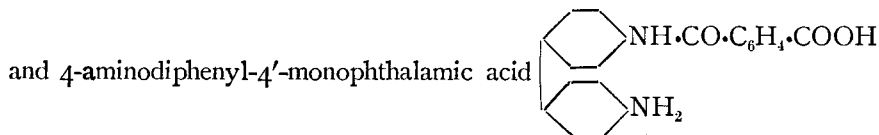
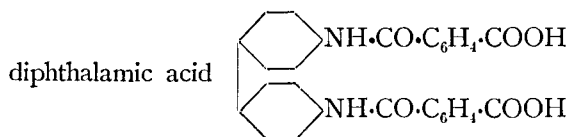
(Found: N = 10.6, C₁₆H₁₆O₂N₂ requires N = 10.5 per cent.).

In benzene solution.— Benzene was substituted for alcohol in the above experiment, and similar results were obtained with a good yield of diacetylbenzidine.

Action of Phthalic Anhydride on Benzidine in Alcoholic Solution.

1.84 gm. (1 mol.) of benzidine was dissolved in 60 c.c. of alcohol and poured into an alcoholic solution of phthalic anhydride, containing 2.96 gm. (2 mols.) of the anhydride in 120 c.c. of alcohol, at the ordinary temperature, followed by vigorous shaking, whereby a white amorphous precipitate soon appeared.

After having been left overnight, the product was filtered, washed with warm alcohol and dried. The yield was about 2.4 gm. The product turned yellow on heating and did not melt completely below 300°. It was found, on titration with alkali,¹ to be a mixture of diphenyl-4:4'-



0.1828 gm. of the substance neutralised 0.0254 gm. NaOH (found);
Diphenyl-4:4'-diphthalamic acid requires 0.0305 gm. NaOH (calc.);
4-Aminodiphenyl-4'-monophthalamic acid

requires 0.0220 gm. NaOH (calc.).

To separate the mixture, it was dissolved in a cold dilute solution of sodium carbonate and treated with carbon dioxide until saturated. A white precipitate came down, which was filtered, washed with water and dried in a vacuum desiccator. It melted and decomposed towards 292–295° and was found to consist chiefly of monophthalamic acid:²

0.2655 gm. of the substance neutralised 0.0331 gm. NaOH (found);
4-Aminodiphenyl-4'-monophthalamic acid

requires 0.0320 gm. NaOH (calc.).

¹ Throughout these experiments, the acid in question was dissolved in cold $n/10$ NaOH and titrated with $n/10$ H_2SO_4 , using phenolphthalein as an indicator.

² The monophthalamic acid is described more fully in the paragraph on "Action of Alkali on Monophthalylbenzidine".

When the sodium carbonate solution above obtained was made acid by dilute acetic acid, a further white precipitate was thrown down, which was found on titration to consist of the diphthalamic acid :

0.1230 gm. of the substance neutralised 0.0209 gm. NaOH (found);
Diphenyl-4 : 4'-diphthalamic acid requires 0.0205 gm. NaOH (calc.).

The diphthalamic acid was easily converted into diphthalylbenzidine on heating. It was insoluble in most organic solvents, but was easily soluble in dilute alkalis forming a salt.

When one molecular proportion each of benzidine and phthalic anhydride in alcoholic solutions were mixed, no precipitation took place even after leaving at the ordinary temperature for a long time.

Action of Phthalic Anhydride on Benzidine in Benzene Solution.

The experiment was carried out in a similar way to that in alcoholic solution, but phthalic anhydride being less soluble in benzene than in alcohol, more of the solvent (150 c.c. for 2.96 gm. of the anhydride) was used, and the addition of the benzidine solution to that of phthalic anhydride was made at about 40° instead of at the room temperature. The reaction product, which formed a white voluminous precipitate, (about 80% yield of the theoretical) consisted chiefly of diphenyl-4 : 4'-diphthalamic acid, after having been well washed with benzene.

0.1541 gm. of the substance neutralised 0.0251 gm. NaOH (found);
Diphenyl-4 : 4'-diphthalamic acid requires 0.0257 gm. NaOH (calc.).
(Found : N = 5.7 (by Kjeldahl method), $C_{25}H_{20}O_6N_2$ requires N = 5.8 per cent.).

Action of Alkali on Diphthalylbenzidine.

Action of NaOH.— Diphthalylbenzidine was prepared according to Bandrowski (Ber., 1884, 17, 1182) by heating phthalic anhydride and benzidine at 200° for three hours.

2 gm. of diphthalylbenzidine were heated in a water bath with 20 c.c. of 10% NaOH solution for two hours, whereby a clear orange yellow solution was ultimately obtained. When the solution was cooled, the sodium salt of diphenyl-4 : 4'-diphthalamic acid came down as an almost colourless crystalline mass, which, when recrystallised from a small quantity of hot water, was obtained in colourless silky needles. After heating at 120° for two hours, the salt was analysed. (Found : Na = 9.0, $C_{25}H_{15}O_6N_2Na_2$ requires Na = 8.8 per cent.).

The free acid was obtained as a white amorphous powder by acidifying the aqueous solution of its sodium salt. Diphenyl-4:4'-diphthalamalic acid thus obtained was identical with that obtained directly from benzidine and phthalic anhydride in benzene or alcoholic solutions.

0.2473 gm. of the substance neutralised 0.0419 gm. NaOH (found); Diphenyl-4:4'-diphthalamalic acid requires 0.0412 gm. NaOH (calc.).

By the above treatment with NaOH, a very small portion of the diphthalybenzidine was also hydrolysed into benzidine and phthalic acid besides the main product of diphenyl-4:4'-diphthalamalic acid.

Action of Na_2CO_3 .— Diphthalybenzidine was only very slightly attacked by prolonged heating (eight hours) in a water bath with 10% Na_2CO_3 solution, about 15% of the substance being converted into the diphthalamalic acid while the main portion remained unchanged.

Diphenyl-4:4'-diphthalamalic acid, like diphthalybenzidine, was completely hydrolysed into benzidine and phthalic acid by heating it with concentrated sulphuric acid at 120-130° for twenty minutes.

Action of Alkali on Monophthalybenzidine.

Monophthalybenzidine was prepared according to Koller (Ber., 1904, **37**, 2882) by heating benzidine and phthalic anhydride in aqueous suspension for eight hours.

When monophthalybenzidine was heated either with 10% NaOH solution or with 10% Na_2CO_3 solution (the latter being preferable in this case, for the caustic alkali is more likely to decompose it into its components) in a water bath for several hours, it was more or less hydrolysed into 4-aminodiphenyl-4'-monophthalamalic acid, but on precipitation of the acid from the alkaline solution, it carried down a certain amount of the acid (acetic or mineral) which could not be removed by repeated washing, thus giving too high a value on titration. It was also observed that the stronger the acid added, the higher the acidity of the precipitated substance, thus hydrochloric acid gave the highest, then sulphuric, and acetic acid the lowest value. It is likely that a certain amount of the acid combines with the free NH_2 -group of the monophthalamalic acid, forming an insoluble salt which comes down with the remainder. Isolation of free 4-amino-diphenyl-4'-monophthalamalic acid, however, was attained by precipitating it from the alkaline solution by passing in carbon dioxide until saturated.

3 gm. of monophthalybenzidine were heated in a water bath with 45 c.c. of 10% Na_2CO_3 solution for five hours, and filtered hot from

1.2 gm. of the unchanged substance. Into the alkaline solution, carbon dioxide was passed until saturated, whereby the monophthalamic acid came down as a white amorphous powder, precipitation being dependent largely on the concentration of the alkaline solution.

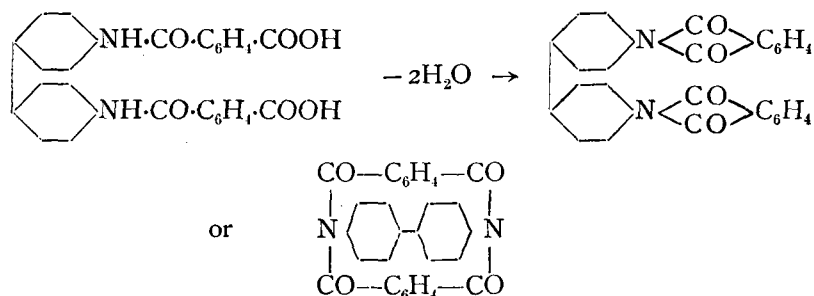
0.0872 gm. of the substance neutralised 0.0105 gm. NaOH (found);
4-Aminodiphenyl-4'-monophthalamic acid

requires 0.0104 gm. NaOH (calc.).

4-Aminodiphenyl-4'-monophthalamic acid, which was insoluble in most organic solvents, darkened on heating and melted with decomposition towards 291–300°. It was not, therefore, converted into monophthalylbenzidine by mere heating.

Dehydration of Diphenyl-4:4'-diphthalamic Acid.

Diphenyl-4:4'-diphthalamic acid was completely converted into diphthalylbenzidine by heating it at 130–140° for two hours in an atmosphere of hydrogen, by losing two molecules of water.



The change of constitution was easily followed by the change of colour, for the original colourless phthalamic acid turned yellow as the transformation proceeded.

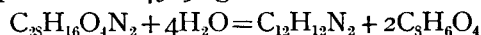
Diphthalylbenzidine thus obtained was crystallised from boiling nitrobenzene, from which it came down in microneedles, and after removal of the nitrobenzene by washing with alcohol and by steam distillation, it was analysed. (Found : N=6.1, C₂₅H₁₆O₄N₂ requires N=6.3 per cent.).

Action of Phthalic Anhydride on Monophthalylbenzidine.

3.14 gm. (1 mol.) of monophthalylbenzidine and 1.48 gm. (1 mol.) of phthalic anhydride were intimately mixed and heated in a sealed tube at about 200° for three and a half hours. Some water was observed to have condensed after the reaction. The product was digested with much boiling alcohol and dried at 80°. As diphthalylbenzidine is known to be

quantitatively hydrolysed into benzidine and phthalic acid by the action of hot sulphuric acid (Bandrowski, *l.c.*), the product was subsequently hydrolysed and the benzidine sulphate formed was weighed.

0.7192 gm. of the substance was heated with 7 grams of concentrated sulphuric acid at 130–140° for twenty minutes and then poured into cold water. After cooling, the separated benzidine sulphate was filtered, washed thoroughly with warm alcohol and with ether to remove any admixed phthalic acid, and finally dried at 120°. Benzidine sulphate thus obtained weighed 0.4565 gm., while the theoretical quantity according to the following equation is 0.4569 gm. :—



Furthermore the product was nitrated with red fuming nitric acid (sp.gr. 1.52/17°), and the nitration product was found to be 3 : 3'-dinitrodiphthalylbenzidine, m.p. 283–284° (with a little 2 : 2'-isomeride) which is also the main product of direct nitration of diphthalylbenzidine (Bandrowski, *l.c.*; Cain, Coulthard and Micklethwait, T., 1912, 101, 2302, T., 1913, 103, 2078 foot note).

From the above experiments it is beyond doubt that the product obtained by the action of another molecule of phthalic anhydride on monophthalylbenzidine is diphthalylbenzidine, identical with that obtained directly by the action of 2 molecules of phthalic anhydride on 1 molecule of benzidine.

Action of Water on 4-Aminodiphenyl-4'-monophthalamic Acid.

As previously stated, 4-aminodiphenyl-4'-monophthalamic acid, unlike diphtalamic acid which is easily converted into diphthalylbenzidine by heating, did not give monophthalylbenzidine on heating but decomposed towards 300°. Monophthalylbenzidine, however, was found to be formed when 4-aminodiphenyl-4'-monophthalamic acid was gently boiled with a large volume of water for several hours, the original colourless phthalamic acid changing gradually to a yellow substance as the boiling proceeded. The yellow product thus obtained was digested with a cold dilute solution of sodium carbonate to remove any unchanged phthalamic acid and then crystallised from boiling nitrobenzene, from which monophthalylbenzidine came down in pale yellow microneedles.

(Found : N = 8.9, $C_{20}H_{14}O_2N_2$ requires N = 8.9 per cent.).

Action of Succinic Anhydride on Benzidine in Solution.

In alcoholic solution.— 1.84 gm. (1 mol.) of benzidine was

dissolved in 50 c.c. of alcohol and was added with stirring at 25° to an alcoholic solution of succinic anhydride, containing 2.0 gm. (2 mols.) of the anhydride in 100 c.c. of alcohol. In a short time, a white precipitate slowly separated. After having been left overnight, the product was filtered, washed with warm alcohol and dried in a vacuum desiccator. The product thus obtained (3.2 gm.), was a white amorphous powder, which did not melt below 300° and was easily soluble in dilute alkalis, from which it was reprecipitated by acid.

0.2255 gm. of the substance neutralised 0.0451 gm. NaOH (found); Diphenyl-4:4'-disuccinamic acid requires 0.0469 gm. NaOH (calc.). (Found: N=7.7, C₂₀H₂₀O₆N₂ requires N=7.3 per cent.).

The slightly higher percentage of N and the lower acidity are most likely due to contamination of a small quantity of 4-aminodiphenyl-4'-monosuccinamic acid probably formed at the same time, which, unlike 4-aminodiphenyl-4'-monophthalamic acid, was not precipitated from the alkaline solution by carbon dioxide.

In benzene solution :— Benzene was substituted for alcohol as a solvent, and the experiment was carried out in the same manner, except that a double portion of the solvent was used for succinic anhydride and the addition was made at 50° instead of 25°. The white amorphous powder, amounting to 86% of the theory, consisted of diphenyl-4:4'-disuccinamic acid.

0.2512 gm. of the substance neutralised 0.0530 gm. NaOH (found); Diphenyl-4:4'-disuccinamic acid requires 0.0523 gm. NaOH (calc.). (Found: N=7.4, C₂₀H₂₀O₆N₂ requires N=7.3 per cent.).

Diphenyl-4:4'-disuccinamic acid was mostly decomposed into benzidine and succinic acid on heating with 10% NaOH solution in a water bath for two hours, while 10% Na₂CO₃ solution had no action at all. Concentrated sulphuric acid (at 120–130° for twenty minutes) also hydrolysed it.

The succinamic acid, unlike the corresponding diphtalamic acid, was not converted into disuccinylbenzidine by heating at 150° for several hours, but gave disuccinylbenzidine at the higher temperature of about 250°.

Action of Succinic Anhydride on Benzidine in Dry State.

At 150°.— 1 mol. of benzidine and a little more than 2 mols. of succinic anhydride were well mixed and heated in a sealed tube at 150° for six hours. The product, after having been thoroughly washed with hot water and boiling alcohol, was found to consist chiefly of diphenyl-4:4'-disuccinamic acid, being almost completely soluble in cold

dilute alkali.

0.2500 gm. of the substance neutralised 0.0517 gm. NaOH (found); Diphenyl-4:4'-disuccinamic acid requires 0.0521 gm. NaOH (calc.).

After having been reprecipitated by hydrochloric acid from its soda solution:

0.2048 gm. of the substance neutralised 0.0430 gm. NaOH (found); Diphenyl-4:4'-disuccinamic acid requires 0.0427 gm. NaOH (calc.).

At 250°.— A similar experiment was conducted at 250°. The greyish white product was digested with boiling alcohol, and then with a cold dilute solution of sodium carbonate to remove all succinamic acid, filtered, washed with water and dried. The product was almost insoluble in most organic solvents, but could be crystallised from boiling aniline in which it is sparingly soluble, and from which it came down in colourless microneedles on cooling. Disuccinylbenzidine thus obtained did not melt below 303°. (Found: N=8.0, $C_{20}H_{16}O_4N_2$ requires N=8.05 per cent.).

Disuccinylbenzidine was only partly converted into diphenyl-4:4'-disuccinamic acid by prolonged heating with dilute soda solution in a water bath, while with 10% NaOH solution, it was mostly hydrolysed into benzidine and succinic acid. Sulphuric and hydrochloric acid, on the other hand, had no effect.

Action of Naphthalic Anhydride on Benzidine.

1 mol. of benzidine and 2 mols. of naphthalic anhydride were heated in an autoclave at 200–210° for four hours. The brown amorphous powder thus obtained was digested with a quantity of boiling alcohol; it dissolved in hot nitrobenzene, from which it separated as a light brown powder on cooling. It did not melt below 305°. (Found: N=5.5 (by Kjeldahl method), Dinaphthalylbenzidine $C_{36}H_{20}O_4N_2$ requires N=5.2, while mononaphthalylbenzidine $C_{24}H_{16}O_2N_2$ requires N=7.7 per cent.). The high percentage of N may be due to contamination with a little mononaphthalylbenzidine formed at the same time. The product was not hydrolysed by concentrated sulphuric acid (at 130° for twenty minutes) or caustic alkali (two hours boiling with 10% NaOH solution).

Action of Diphenic Anhydride on Benzidine in Benzene Solution.

1.38 gm. (1 mol.) of benzidine was dissolved in 50 c.c. of benzene and added with stirring at 60° to a diphenic anhydride solution, containing 3.36 gm. (2 mols.) of the anhydride in 250 c.c. of benzene. A turbidity

soon appeared and precipitation of a white amorphous powder gradually took place. After being left to stand at the room temperature for two days, the product was filtered, digested with hot benzene and dried in a vacuum desiccator. The white, amorphous powder, thus obtained, (3.9 gm.) melted towards 180° with apparent decomposition. It was easily soluble in dilute alkalis and in warm alcohol. It appeared to be a mixture of di- and mono-diphenamic acids, judging from the result of titration with alkali:

0.1859 gm. of the substance neutralised 0.0212 gm. NaOH (found); Diphenyl-4:4'-di-diphenamic acid requires 0.0235 gm. NaOH (calc.); 4-Aminodiphenyl-4'-mono-diphenamic acid requires 0.0182 gm. (calc.).

Isolation of di-diphenamic acid was effected by dissolving the mixture in a dilute solution of alkali and precipitating the acid with hydrochloric acid, in which the mono-diphenamic acid is apparently soluble.

2.4811 gm. of the mixture, separated from the benzene solution, was dissolved in a cold dilute solution of sodium hydroxide. Dilute hydrochloric acid was added with stirring until the solution became acid, whereby a white voluminous precipitate came down. The whole was warmed in a water bath, filtered and washed with warm water. The residue, which contained no hydrochloric acid, amounted to 1.8875 gm. when dried, melting towards 165° with decomposition, and was found to be diphenyl-4:4'-di-diphenamic acid by titration and analysis:

0.1885 gm. of the substance neutralised 0.0238 gm. NaOH (found); Diphenyl-4:4'-di-diphenamic acid requires 0.0239 gm. NaOH (calc.). (Found: $N=4.3$, $C_{40}H_{28}O_6N_2$ requires $N=4.4$ per cent.).

Hot concentrated hydrochloric acid and 10% NaOH solution had no hydrolysing action on diphenyl-4:4'-di-diphenamic acid.

When sufficient sodium acetate was added to the filtrate from the above to remove free hydrochloric acid, a further quantity of flocculent precipitate was thrown down, which was filtered, washed with cold water and dried in a vacuum desiccator. It amounted only to 0.1624 gm. shrinking on heating and melting towards 215° .

0.0545 gm. of the substance neutralised 0.0059 gm. NaOH (found), which amount rather agreed with the theoretical quantity of alkali, *i. e.* 0.0053 gm. NaOH, required by 0.0545 gm. of 4-aminodiphenyl-4'-mono-diphenamic acid, but as the quantity of the sample was very small, little reliance can be attached to this result.

On heating 2 mols. of diphenic anhydride and 1 mol. of benzidine at 200° for five hours in a sealed tube, a dark-coloured fused mass was formed, which was probably a mixture of mono- and di-diphenamic

acids, but was not further investigated owing to the difficulty of purification.

The author wishes to express his thanks to his father, Dr. Kotaro Shimomura, at whose instigation the above work was carried out, for his keen interest in the research and many valuable suggestions.