CCCLVIII.—*Investigations in the Diphenyl Series. Part II. Substitution Reactions.*

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THE dinitration of diphenyl has been described by Fittig (*Annalen*, 1862, **124**, 276), Schultz (*Annalen*, 1874, **174**, 201), and Willstätter (*Ber.*, 1906, **39**, 3478), the products isolated being 4 : 4′- and 2 : 4′-dinitrodiphenyls. Schultz and Strasser (*Ber.*, 1881, **14**, 612) record that 2-nitrodiphenyl on re-nitration gives 2 : 4′-dinitrodiphenyl. The nitration of 4-nitrodiphenyl does not appear to have been described. It has now been found that both in the dinitration of diphenyl and in the nitration of 2-nitrodiphenyl there are also produced considerable quantities of 2 : 2′-dinitrodiphenyl; under similar conditions 4-nitrodiphenyl gives 2 : 4′- and 4 : 4′-dinitrodiphenyls. The non-formation of any considerable quantity of 2 : 4-dinitrodiphenyl in these various reactions is somewhat surprising.

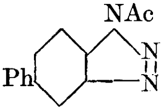
The isolable products of the nitration of 4-benzylideneaminodiphenyl in sulphuric acid solution are soluble in ammonia—an indication that simultaneous sulphonation has taken place. By using a smaller proportion of sulphuric acid a small yield of 4′-nitro-4-aminodiphenyl is obtained. This result is in marked contrast to the facile nitration of 4-acetylaminodiphenyl and of 4-dimethylaminodiphenyl, which give only the 3-nitro-derivatives (compare Fichter and Sulzberger, *Ber.*, 1904, **37**, 878; Garciá Banús and Ferrer Tomás, *Anal. Fís. Quím.*, 1921, **19**, 293). Since 4-hydroxydiphenyl on energetic nitration gives 3 : 5 : 4′-trinitro-4-hydroxydiphenyl (Garciá Banús and Guiteras, *Anal. Fís. Quím.*, 1923, **21**, 126) whilst 4-acetylaminodiphenyl on chlorination (bromination) gives 3 : 5 : 4′-trichloro(tribromo)-4-acetylaminodiphenyl (Scarborough and Waters, this vol., p. 557), the alleged conversion of 3-nitro-4-dimethylaminodiphenyl into 3 : 5 : 2′ : 4′-tetranitro-4-dimethylaminodiphenyl by further nitration (Garciá Banús and Ferrer Tomás, *loc. cit.*) seemed very striking. It has now been found that this product is a dinitro-4-nitrosomethylaminodiphenyl.

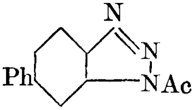
Its constitution has been confirmed by its preparation from 4-nitrosomethylaminodiphenyl.

Nitration of 3-nitro-4-dimethylaminodiphenyl in sulphuric acid solution gives a dinitro-derivative, m. p. 137—138°. This is probably identical with the dinitro-compound, m. p. 134°, believed by Vorländer (*Ber.*, 1925, **58**, 1909) to be 3 : 4′-dinitro-4-dimethylaminodiphenyl. Addition of one molecular proportion of nitric acid to a solution of 4-dimethylaminodiphenyl in sulphuric acid produces a mononitro-monosulphonic acid together with a small proportion of the dinitrated amine.

3 : 4-Diaminodiphenyl has been obtained in greatly improved yield and some of its derivatives have been examined. 3-Amino-4-acetylaminodiphenyl reacts with nitrous acid to give 1-*acetyl*-5-*phenyl*-1 : 2 : 3-*benztriazole* (I), which was also obtained together with 1-*acetyl*-6-*phenyl*-1 : 2 : 3-*benztriazole* (II) by the acetylation of 5 (or 6)-phenyl-1 : 2 : 3-benztriazole.

(I.)





(II.)

On adding sodium nitrite to a solution of tetramethylbenzidine in hydrochloric acid Michler and Pattinson (*Ber.*, 1881, **14**, 2164) obtained a dinitro-derivative, m. p. 188°, which gave a diamine, m. p. 168°, on reduction. Garciá Banús and Ferrer Tomás (*loc. cit.*) had difficulty in repeating this experiment and even by an improved method obtained only a product of m. p. 181—183°. By replacing the hydrochloric acid by acetic acid we have obtained an almost quantitative yield of the dinitro-compound of m. p. 188°. Ullmann and Dieterle (*Ber.*, 1904, **37**, 23) prepared 2 : 2′-dinitrotetramethylbenzidine (m. p. 230°), by nitrating the amine in sulphuric acid solution, and from it the corresponding diamine, m. p. 166°. The two diamines are not identical, as has been shown by the melting point of a mixture of the two and by the properties of their diacetyl derivatives. 2-Nitrotetramethylbenzidine is converted by the action of sodium nitrite and acetic acid into a dinitro-derivative, m. p. 145°, which is almost certainly 2 : 3′-dinitrotetramethylbenzidine. It thus appears highly probable that Michler and Pattinson's dinitro-compound is 3 : 3′-dinitrotetramethylbenzidine. An attempt to synthesise this compound by Ullmann's method was unsuccessful, probably owing to the fact that these compounds decompose slightly above their melting points.

In continuation of the work recorded in Part I (this vol., p. 1239) the hydrolysis of 4-benzoyloxy-4′-acetylaminodiphenyl has been examined. The result is in complete agreement with that recently published by Raiford and Clark (*J. Amer. Chem. Soc.*, 1926, **48**, 483)—4-hydroxy-4′-acetylaminodiphenyl is produced without any trace of 4-hydroxy-4′-benzoylaminodiphenyl. This result does not seem to be in harmony with the Kaufler formula for diphenyl, which, moreover, would require that mono-substituted derivatives such as 2-aminodiphenyl should be capable of exhibiting optical isomerism. No case of this kind is recorded in the literature and, as shown in the experimental part, the brucine and morphine salts of diphenyl-2-carboxylic acid have been repeatedly crystallised from various solvents without any indication of resolution being observed.

EXPERIMENTAL.

Nitration of Diphenyl.—Diphenyl (20 g.), dinitrated by Willstätter's method (*loc. cit.*), gave 4 : 4′-dinitrodiphenyl (6·7 g.) and a more soluble fraction (14·5 g.), m. p. 70—80°, which, after five recrystallisations from alcohol, gave pure 4 : 2′-dinitrodiphenyl. The solid obtained after evaporation of the alcoholic mother-liquors was crystallised four times from benzene, and the pure 2 : 2′-dinitrodiphenyl, m. p. 127—128°, thus obtained was compared with 2 : 2′-dinitrodiphenyl prepared from *o*-chloronitrobenzene by Ullmann's method (*Ber.*, 1901, **34**, 2177).

Nitration of 2-Nitrodiphenyl.—A mixture of 2-nitrodiphenyl (20 g.), fuming nitric acid (14 c.c.), and water (2 c.c.), having been gently warmed for ½ hour, was poured into water. The precipitated semi-solid material was filtered to remove unchanged 2-nitrodiphenyl (1·5 g.) and the residual solid (21 g.) was separated by the method described above into 4 : 2′- and 2 : 2′-dinitrodiphenyls.

Nitration of 4-Nitrodiphenyl.—4-Nitrodiphenyl (20 g.), after being nitrated and worked up by the procedure described above, gave 4 : 4′-dinitrodiphenyl (11·4 g.) and a more soluble product (11 g.) from which, after many recrystallisations, pure 4 : 2′-dinitrodiphenyl was isolated. 2′-*Nitro-4-dimethylaminodiphenyl*, prepared by shaking together 2′-nitro-4-aminodiphenyl, methyl sulphate, and sodium hydroxide solution, crystallised from alcohol in small, crimson needles, m. p. 100° (Found : C, 69·6; H, 5·6. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%). The 2′-nitro-4-aminodiphenyl was obtained in poor yield by the action of ammonium sulphide on an alcoholic solution of 2′ : 4-dinitrodiphenyl.

4-*Benzylideneaminodiphenyl* was obtained, by the addition of benzaldehyde (1 mol.) to a boiling ethyl-alcoholic solution of 4-aminodiphenyl, in bulky, lustrous plates, m. p. 148° (Found : N, 5·55. $C_{19}H_{15}N$ requires N, 5·45%). To this compound (8·6 g.), suspended in sulphuric acid (13 c.c.), a mixture of nitric acid (3 c.c.) and sulphuric acid (2 c.c.) was added, and the liberated benzaldehyde removed in a current of steam. The residual mixture was made alkaline, and the solid repeatedly crystallised from alcohol until the melting point became constant at 200° (4′-nitro-4-aminodiphenyl).

3-*Nitro*-4-p-*toluenesulphonylaminodiphenyl.*—4-*p*-Toluenesulphonylaminodiphenyl (6 g.) was warmed for 9 hours with a mixture of nitric acid (5 c.c.) and water (100 c.c.). The product (6·5 g.) crystallised from alcohol in long, yellow needles, m. p. 118° (rather indefinite) (Found: C, 62·0; H, 4·4. $C_{19}H_{16}O_4N_2S$ requires C, 61·9; H, 4·35%). By hydrolysis with 75% sulphuric acid at 100°, pure 3-nitro-4-aminodiphenyl was obtained.

3-*Nitro*-4-*acetylaminodiphenyl.*—4-Acetylaminodiphenyl was nitrated by Fichter and Sulzberger's method (*loc. cit.*). The crude product melted at 125—128° (yield, more than 90%). Crystallised from alcohol, in which it was completely soluble (thus indicating the absence of 3 : 5-dinitro-4-acetylaminodiphenyl), it gave pure 3-nitro-4-acetylaminodiphenyl, m. p. 132°; the mother-liquor contained 3-nitro-4-aminodiphenyl.

3 : 4-*Diaminodiphenyl* was prepared by adding aluminium amalgam to a suspension of 3-nitro-4-aminodiphenyl in moist ether until the red particles had disappeared. After removal of the aluminium hydroxide and evaporation of the ether, the residual diamine crystallised from alcohol in small, colourless cubes, m. p. 103° (yield, 70%) (Found: N, 14·9. Calc.: N, 15·2%).

Acetic anhydride converted the diamine into 3 : 4-*diacetyldiaminodiphenyl*, m. p. 163°. A solution of this compound in aqueous alcohol set to a thick, clear jelly which, after 24 hours, was completely transformed into compact, colourless needles (Found: N, 10·4. $C_{16}H_{16}O_2N_2$ requires N, 10·4%). The diamine was converted by benzoyl chloride and sodium hydroxide into 3 : 4-*dibenzoyldiaminodiphenyl*, which melted at 248° after being boiled with alcohol, in which it was almost insoluble (Found: N, 6·8. $C_{26}H_{20}O_2N_2$ requires N, 7·1%). 3 : 4-Diaminodiphenyl condensed with benzil in acetic acid solution to give the *quinoxaline* derivative, which separated from alcohol as a yellow, crystalline powder, m. p. 148° (Found: N, 7·9. $C_{26}H_{18}N_2$ requires N, 7·8%).

3-*Amino*-4-*acetylaminodiphenyl* was prepared by adding aluminium amalgam to a suspension of 3-nitro-4-acetylaminodiphenyl (25 g.) in moist ether (1·5 litres) until the yellow colour had disappeared. The ether was evaporated, and the residue extracted several times with boiling alcohol. The hot alcoholic extracts were concentrated, filtered, and cooled, the compound (17 g.) being then deposited in colourless platelets, m. p. 155° (Found: C, 74·5; H, 6·2. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2%). By the action of acetic anhydride and of benzoyl chloride and sodium hydroxide it was converted into 3 : 4-diacetyldiamino- and 3 : 4-dibenzoyldiamino-diphenyl (described above) respectively. Benzoyl chloride reacted with a pyridine solution to give 3-*benzoylamino*-4-*acetylaminodiphenyl*, which separated as a white, crystalline powder, m. p. 186°, from alcohol (Found : N, 8·35. $C_{21}H_{18}O_2N_2$ requires N, 8·5%).

1-*Acetyl*-5-*phenyl*-1 : 2 : 3-*benztriazole* (I) was obtained by adding sodium nitrite (3·5 g.), dissolved in water, to a stirred solution of 3-amino-4-acetylaminodiphenyl (11·3 g.) in hydrochloric acid (12·5 c.c.) and water (300 c.c.). The dried precipitate separated from alcohol (300 c.c.) in fine, silky needles (6·4 g.), m. p. 130—132° (Found : Ac, 18·3. $C_{14}H_{11}ON_3$ requires Ac, 18·2%). 5 (or 6)-Phenyl-1 : 2 : 3-benztriazole (3·1 g.) was obtained from the alcoholic filtrate as a white, crystalline powder, m. p. 156° (Found : C, 73·4; H, 4·4; N, 21·1. Calc. : C, 73·8; H, 4·6; N, 21·8%). This triazole is readily soluble in sodium hydroxide solution and can be titrated with approximate accuracy, thymolphthalein being used as indicator (Found : M, 199. Calc. : M, 195).

By the action of acetic anhydride or acetyl chloride on its solution in pyridine it gives a mixture of the two possible acetyl derivatives (I and II) which, on account of their similar solubility, are difficult to separate, and it is not certain that (II) has been obtained pure. They each form needles, (I) m. p. 130—132°, (II) m. p. 97°. On heating (I) with acetic anhydride a mixture of (I) and (II), m. p. 92—97°, is obtained. The great stability of the linking of two of the three nitrogen atoms present in the molecules of these compounds is shown by the results of the estimation of nitrogen by Kjeldahl's method [Found : (I) N, 5·9, 6·0; (II) N, 5·9. $C_{14}H_{11}N_3$ requires N, 17·7 (= 3 × 5·9%). Found for 5 (or 6)-phenyl-1 : 2 : 3-benztriazole : N, 7·0, 7·1, 7·1. Calc. : N, 21·5 (= 3 × 7·16%)].

3-*Amino*-4-*benzoylaminodiphenyl*, prepared by the reduction of 3-nitro-4-benzoylaminodiphenyl with aluminium amalgam (compare preparation of 3-amino-4-acetylaminodiphenyl), melts at 221° (Found : N, 9·6. $C_{19}H_{16}ON_2$ requires N, 9·7%). It is difficultly soluble in acids and only moderately easily soluble in boiling alcohol. It reacts with acetic anhydride to give 3-*acetylamino*-4-*benzoylaminodiphenyl*, which crystallises from alcohol as a white powder, m. p. 211° (Found : N, 8·5. $C_{21}H_{18}O_2N_2$ requires N, 8·5%), and with benzoyl chloride and sodium hydroxide to give 3 : 4-dibenzoyldiaminodiphenyl (above).

4-*Dimethylaminodiphenyl*, prepared by shaking 4-aminodiphenyl with methyl sulphate and sodium hydroxide, crystallises from alcohol in lustrous, white plates, m. p. 123°. Diphenylyltrimethylammonium hydroxide, which is formed in considerable quantity during the reaction, is best isolated as the bromide, m. p. 222°, by the addition of potassium bromide to the filtrate (Vorländer, *loc. cit.*).

When 4-aminodiphenyl is heated under reflux with sodium carbonate and methyl iodide (1 mol.), a considerable quantity of 4-dimethylaminodiphenyl methiodide, m. p. 218° (decomp.), is formed, so that this method possesses no advantage over the preceding one when the tertiary base is required.

3-*Nitro*-4-*dimethylaminodiphenyl*.—An excess of a solution of sodium nitrite was added to 4-dimethylaminodiphenyl (16·5 g.) in acetic acid, and the red crystals which gradually separated were recrystallised from methyl alcohol; they then melted at 74° (14·5 g.). Dilution of the acetic acid filtrate with water gave a further crop of the same crystals. On the other hand, the continued addition of sodium nitrite gave pale yellow crystals, m. p. 122° (compare below).

3-Nitro-4-dimethylaminodiphenyl does not combine with methyl iodide even at 100° in a sealed tube. Reduction of an ethereal solution by aluminium amalgam gave only crude 3-amino-4-dimethylaminodiphenyl, which was very difficult to purify. On warming this crude product with acetic anhydride, 3-*acetylamino*-4-*dimethylaminodiphenyl* was obtained which crystallised readily from alcohol in felted needles, m. p. 167° (Found : C, 75·5; H, 7·0. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·1%). 5-Phenyl-1 : 2-dimethylbenziminazole was not produced when this compound was boiled with acetic anhydride (compare Pinnow, *Ber.*, 1899, **32**, 1666).

3 : (5 ?)-*Dinitro*-4-*nitrosomethylaminodiphenyl*.—(a) Fuming nitric acid (5 c.c.) was added to 3-nitro-4-dimethylaminodiphenyl (9·6 g.), dissolved in warm acetic acid (60 c.c.), and after ½ hour the mixture was allowed to cool; pale yellow needles, m. p. 122°, were then obtained. The mother-liquor was poured into water, and the precipitate thus formed was crystallised from alcohol; after separation of a small amount of difficultly soluble material (m. p. 290—292°), a further crop of *dinitro*-4-*nitrosomethylaminodiphenyl* was obtained (Found: C, 51·9; H, 3·5; N, 18·6. $C_{13}H_{10}O_5N_4$ requires C, 51·7; H, 3·3; N, 18·5%).

(b) To 4-nitrosomethylaminodiphenyl (3 g.), dissolved in warm acetic acid (20 c.c.), fuming nitric acid (2 c.c.) was added. On cooling, lustrous needles, m. p. 122°, separated, identical with the product obtained by method (a).

3 : (5 ?)-*Dinitro*-4-*methylaminodiphenyl*.—Dinitro-4-nitrosomethylaminodiphenyl (4·5 g.) was heated under reflux with alcoholic hydrogen chloride (100 c.c.). The bright red needles thus obtained in theoretical yield melted at 142—143° after being boiled with

alcohol (Found : C, 57·3; H, 4·2. $C_{13}H_{11}O_4N_3$ requires C, 57·1; H, 4·0%). The substance was unchanged after boiling with acetic anhydride for 1 hour (compare Kauffmann, *Ber.*, 1907, **40**, 4006), but in warm acetic acid was rapidly reconverted into the nitroso-derivative on addition of sodium nitrite.

3 : (4′ ?)-*Dinitro-4-dimethylaminodiphenyl.*—3-Nitro-4-dimethylaminodiphenyl (2·42 g.) was dissolved in sulphuric acid (40 c.c.), and nitric acid (3·8 c.c.) added drop by drop. After 3 hours, the mixture was poured on to ice, the product neutralised with ammonia, and the precipitate crystallised several times from alcohol, orange-red plates, m. p. 137—138°, being obtained (Found : C, 58·5; H, 4·3. $C_{14}H_{13}O_4N_3$ requires C, 58·6; H, 4·5%).

Nitration of 4-Dimethylaminodiphenyl in Sulphuric Acid Solution.—The nitration (4-dimethylaminodiphenyl, 2·7 g.; sulphuric acid, 20 c.c.; nitric acid, 1·1 c.c.) and the subsequent treatment were as described above. The pasty precipitate was separated from the alkaline liquid, dried, and extracted with benzene, which removed a very small quantity of a deep red, crystalline compound [probably 2 : 4′(?)-dinitro-4-dimethylaminodiphenyl], m. p. 170—171° (Found : C, 58·7; H, 4·7. $C_{14}H_{13}O_4N_3$ requires C, 58·6; H, 4·5%). The part insoluble in benzene crystallised from alcohol in orange plates, m. p. 215—217°, which contained sulphur and evolved ammonia when heated with dilute alkali (Found : C, 49·1; H, 4·8. $C_{14}H_{17}O_5N_3S$ requires C, 49·5; H, 5·0%). This compound dissolved in warm dilute hydrochloric acid, and, on cooling, long, colourless needles separated which did not melt at 300°. Owing to the explosive character of this derivative, analysis by combustion proved useless. The yield of dinitro-4-dimethylaminodiphenyl was not increased by the use of 2 mols. of nitric acid in its preparation.

2 : 2′-*Diaminotetramethylbenzidine*, prepared by Ullmann and Dieterle's method (*loc. cit.*), crystallised from alcohol in plates, m. p. 166°. With acetic anhydride, it yielded the *diacetyl* derivative, which crystallised in fine, white leaflets, m. p. 191—192°, from aqueous alcohol (Found : C, 67·6; H, 7·2. $C_{20}H_{26}O_2N_4$ requires C, 67·8; H, 7·3%).

2-*Nitrotetramethylbenzidine.*—A mixture of tetramethylbenzidine (9·6 g.), sulphuric acid (140 c.c.), and nitric acid (2·8 c.c.), after being kept for 8 hours, was poured on to ice, and neutralised with ammonia. The dried product (m. p. 160°) crystallised from benzene as a dull red, crystalline powder, m. p. 164° (Found : C, 67·5; H, 6·8. $C_{16}H_{19}O_2N_3$ requires C, 67·4; H, 6·7%). The constitution of this compound follows from the fact that on further nitration it yields 2 : 2′-dinitrotetramethylbenzidine.

2 : (3′ ?)-*Dinitrotetramethylbenzidine.*—Sodium nitrite (2 g.) in

water (5 c.c.) was added to a solution of 2-nitrotetramethylbenzidine (2 g.) in cold acetic acid (60 c.c.). The precipitate thus formed crystallised from benzene–ligroin as a brilliant red powder, m. p. 145° (Found : C, 58·4 ; H, 5·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2 ; H, 5·4%).

(3 : 3′ ?) - *Dinitrotetramethylbenzidine.* — To tetramethylbenzidine (4·8 g.), dissolved in cold acetic acid (75 c.c.), was added a solution of sodium nitrite (4 g.) in water (10 c.c.). The solution assumed a deep green colour, but towards the end of the reaction this faded and the liquid filled with an orange precipitate, which crystallised from benzene in light red needles, m. p. 188°. The corresponding diamine, obtained by the same method as 2 : 2′-diaminotetramethylbenzidine, crystallised from alcohol in plates, m. p. 165—166° (mixed with 2 : 2′-diaminotetramethylbenzidine, it melted at 135°). With acetic anhydride, it gave a *diacetyl* derivative which separated from much alcohol as a white, crystalline powder, m. p. 281—282° (Found : C, 68·0 ; H, 7·3. $C_{20}H_{26}O_2N_4$ requires C, 67·8 ; H, 7·3%).

In an attempt to prepare tetranitrotetramethylbenzidine, 2 : 2′-dinitrotetramethylbenzidine (3·3 g.) was dissolved in sulphuric acid (40 c.c.), and nitric acid (1·5 c.c.) added. On being worked up in the usual way, the major part of the substance was recovered unchanged, but a small fraction, m. p. 185°, was obtained (Found : C, 50·8 ; H, 4·4%). This may be a trinitrotetramethylbenzidine ($C_{16}H_{17}O_6N_5$ requires C, 51·2 ; H, 4·5%).

Attempted Synthesis of the Dinitrotetramethylbenzidines.—The nitration of 4-iododimethylaniline (prepared by Baeyer's method, *Ber.*, 1905, **38**, 2762) proved unsuccessful, as either iodine was eliminated or blue products were formed (compare Merz and Weitz, *Ber.*, 1877, **10**, 746).

4-*Bromo*-3-*nitrodimethylaniline* was prepared (*a*) by the nitration of 4-bromodimethylaniline in the cold, (*b*) by the bromination of 3-nitrodimethylaniline (Ephraim and Hochuli, *Ber.*, 1915, **48**, 630). Although the yield obtained by method (*a*) was good, the product was accompanied by a trace of a substance which was removed with difficulty; this crystallised in short, crimson needles, m. p. 109—111°, from alcohol and was probably 4-bromo-3 : 5-dinitrodimethylaniline. Method (*b*) gave at once pure 4-bromo-3-nitrodimethylaniline, m. p. 95°. When this was heated with copper powder, an explosive reaction took place at about 170°. No reaction took place on prolonged boiling with copper powder in toluene—the absence of reaction might have been expected, since 4-bromo-3-nitrodimethylaniline was unchanged after heating under reflux with piperidine for 1½ hours.

4-*Benzylideneamino* -4′ - *hydroxydiphenyl.*—4-Amino - 4′ - hydroxydiphenyl (5 g.) was warmed with benzaldehyde and alcohol (200 c.c.).

On cooling, the solution deposited plates, m. p. 200° (Found : N, 5·3. $C_{19}H_{15}ON$ requires N, 5·15%).

4-*Acetylamino-4′-acetoxydiphenyl*.—4-Amino - 4′- hydroxydiphenyl was heated under reflux for 5 hours with a mixture of acetic anhydride and acetic acid. The product, recrystallised from acetic acid, formed plates, m. p. 218—220°. On prolonged keeping in pyridine solution with benzoyl chloride (1 mol.), it gave 4-*acetylbenzoylamino-4′-acetoxydiphenyl*, which crystallised from alcohol in large, compact plates, m. p. 142—143° (Found: C, 73·9; H, 5·3. $C_{23}H_{19}O_4N$ requires C, 74·0; H, 5·1%). On hydrolysis with alcoholic sodium hydroxide this yielded 4-benzoylamino-4′-hydroxydiphenyl, which was also prepared by the addition of benzoyl chloride (1 mol.) to a solution of 4-amino-4′-hydroxydiphenyl in pyridine.

2-*Aminodiphenyl* was prepared by the method of Aeschlimann, Lees, McClelland, and Nicklin (J., 1925, **127**, 67). Owing to its feebly basic character, no suitable salts with optically active acids could be obtained.

Diphenyl-2-carboxylic acid, obtained by Pictet and Ankeromit's method (*Annalen*, 1891, **266**, 143), formed well-defined brucine and morphine salts, which were crystallised from several solvents, without, however, any indication of resolution being obtained. The strychnine and the quinine salts were obtained as viscous oils which could not be crystallised.

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