

CCCC.—*Substitution Products of 3-Nitro- and 3-Amino-diphenyl.*

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THE study of the orientation of substituents in 2-amino- and in 4-amino-diphenyl and in their acetyl derivatives (J., 1926, 557; this vol., pp. 89, 1133) has now been extended to a consideration of the substitution products of 3-nitro- and of 3-amino-diphenyl. The inclusion of 3-nitrodiphenyl in the scope of the work makes it possible to compare the behaviour of the three possible mononitrodiphenyls as well as the three monoaminodiphenyls.

The chlorination of 3-nitrodiphenyl took place readily in the presence of a powerful catalyst and at moderately high temperatures. The product was a mixture of compounds, containing one to four atoms of chlorine per molecule, the composition of which depended on the temperature and the duration of the chlorination. From these mixtures, 4'-chloro-, 2' : 4'-dichloro-, a tri- and a tetrachloro-3-nitrodiphenyl were isolated. Isomeric mono- and dichlorination products could not be isolated from the semi-solid matter deposited on slow evaporation of the crystallising media. A structure has not been assigned to the higher chlorination products, although the evidence indicated that 2' : 4' : 5-trichloro- and 2' : 4' : 5 : 6'-tetrachloro-3-nitrodiphenyl had been isolated. The possibility that a chlorine atom was substituted in the 2-, 4-, or 6-position seems to be excluded, since piperidine did not react with either of these compounds (compare Le Fèvre and Turner, this vol., p. 1113).

3-Nitrodiphenyl on bromination yielded 4'-bromo-3-nitrodiphenyl as the sole product. The introduction of a second bromine atom could not be effected under the most drastic conditions.

The nitration of 3-nitrodiphenyl in fuming nitric acid solution yielded a mixture of 3 : 4'- and 2' : 3-dinitrodiphenyl. Further nitration, in sulphuric acid solution, of each of these isomerides led to the same product; and since this product on treatment with piperidine yielded 2' : 3 : 4'-trinitro-4-piperidinodiphenyl (Le Fèvre and Turner, J., 1926, 2041), it must have the structure 2' : 3 : 4 : 4'-tetranitrodiphenyl. Attempts were made to prepare a trinitrodi-

phenyl, but the product proved to be a mixture which could not be separated into its constituents.

The direct chlorination of 3-aminodiphenyl in glacial acetic acid and in carbon tetrachloride solution gave black, resinous masses which were not further investigated. 3-Acetamidodiphenyl, however, gave a stable *N-chloroamine* which could be converted, on treatment with alcohol and acetic acid, into 4-chloro-3-acetamidodiphenyl. The same product was obtained by direct chlorination of 3-acetamidodiphenyl in glacial acetic acid solution. An unstable *N-chloroamine* was obtained by treating 4-chloro-3-acetamidodiphenyl with sodium hypochlorite; the evolution of free chlorine from this compound may be taken as an indication that a second chlorine atom cannot be introduced into either nucleus by the indirect method.

Bromination of the free base in carbon tetrachloride solution yielded 4-bromo-3-aminodiphenyl hydrobromide and after prolonged treatment 2 : 4 : 6-tribromo-3-aminodiphenyl. In acetic acid solution bromination of the free base gave a quantitative yield of 2 : 4 : 6-tribromo-3-aminodiphenyl. Under the usual experimental conditions, 3-acetamidodiphenyl did not yield an *N-bromoamine*. Direct bromination of the acetyl derivative in glacial acetic acid solution at the ordinary temperature gave a nearly quantitative yield of 4-bromo-3-acetamidodiphenyl; in the presence of excess bromine and at 100—120°, 4 : 6-dibromo-3-acetamidodiphenyl was obtained. Higher bromination products did not appear to be formed.

On nitration of 3-acetamidodiphenyl in a mixture of glacial acetic acid and acetic anhydride at 70°, 4-nitro-3-acetamidodiphenyl was isolated in an approximately 50% yield; the residue was a viscid oil from which a crystalline compound could not be obtained. Nitration of 3-acetamidodiphenyl and of 4-bromo-3-acetamidodiphenyl in fuming nitric acid solution yielded 4'-nitro-3-acetamidodiphenyl and 4-bromo-4'-nitro-3-acetamidodiphenyl, respectively.

A comparison of the results obtained on the introduction of a further substituent into the isomeric mononitrodiphenyls shows that there is a great similarity of behaviour. Thus in each case further substitution takes place in the 2'- or the 4'-position of the unsubstituted nucleus. Bromination yields one product only, the bromine atom entering the 4'-position, and further bromination cannot be effected (compare Turner and Le Fèvre, J., 1926, 2041). The nitration of each of the isomerides yields two dinitrodiphenyls, the entering group substituting in the 2'- or the 4'-position. The relative proportion in which these isomerides are formed appears to vary with the position of the nitro-group originally present, since

3-nitrodiphenyl yields a much higher percentage of a product substituted in the 4'-position than does 4-nitrodiphenyl (compare Bell and Kenyon, J., 1926, 2705). The formation of 2':3:4:4'-*tetranitrodiphenyl*, in almost quantitative yield, by the further nitration of 2':3- and of 3:4'-dinitrodiphenyl is of considerable interest, since compounds having this orientation of their substituents may be obtained from widely different starting points; thus 4-bromo-2'-nitro-, 4-bromo-4'-nitro-, and 4:4'-dibromo-diphenyl yield products of this type on nitration.

A comparison of the substitution products of the isomeric mono-aminodiphenyls shows that bromination can be carried out progressively until each position in the *op*-relationship to the amino-group has been substituted. The *p*-position to the amino-group is not necessarily the first position to be attacked, as will be seen from a comparison of 2- and 3-aminodiphenyl.

The acetyl derivatives of the three bases form stable *N*-chloroamines which may be converted into nuclear-substituted compounds, but in each case one chlorine atom only may be introduced by this method. Direct halogenation of the acetyl derivatives cannot be carried as far as in the case of the free bases, one position in the ring containing the acetamido-group resisting substitution.

The product isolated on nitration of any of the acetyl derivatives in fuming nitric acid solution or in solution in a strong mineral acid is one substituted in the 4'-position, whereas the product isolated on nitration in acetic acid solution is one substituted in the ring containing the acetamido-group.

4-Acetamidodiphenyl appears to differ from its isomerides in that bromination in the 4'-position can take place without previous substitution in the 3-position.

In a previous communication (J., 1926, 557), tentative rules for the orientation of substituents in the diphenyl series were proposed. The increased data now available show that but little modification of those rules is needed. It was assumed that the linkage between the two nuclei of diphenyl was of such a nature that either phenyl group, like all other hydrocarbon residues, acted as a negative (*op*-directive) group. It now seems well established that the directive power of the phenyl group is appreciably less than that due to the acetamido-group, but is greater than that due to chlorine or bromine.

The directive power of the groups  $C_6H_4X$  and  $C_6H_3XY$  depends on the nature of the substituents X and Y: when X or Y inhibits further substitution in the nucleus in which it occurs, the directive power of the group as a whole will be decreased, and this decrease becomes more marked when X or Y is a positive group.

## E X P E R I M E N T A L.

*3-Nitrodiphenyl*.—Bamberger's method (*Ber.*, 1896, 29, 446; see also Jacobsen, *Ber.*, 1903, 36, 4083; Gomberg, *J. Amer. Chem. Soc.*, 1924, 46, 2339; 1926, 48, 1372), slightly modified, was found to be the most economical for the preparation in bulk. A paste of 50 g. of *m*-nitroaniline and 80 c.c. of concentrated hydrochloric acid was treated with a solution of 35 g. of sodium nitrite in 100 c.c. of water. Frothing was diminished by the addition of thiophen-free benzene, the volume of which was made up to 300 c.c. on completion of the reaction. This mixture was made alkaline with a 15% solution of sodium hydroxide (*ca.* 300 c.c., added drop by drop) and then acidified with glacial acetic acid. The whole series of operations was carried out below 5° and with vigorous stirring. The semi-solid mass was heated on the water-bath for 30 minutes, the sodium acetate removed, and the benzene layer separated from the aqueous layer and treated with benzene-light petroleum (b. p. 40–60°) to precipitate tar. The clear liquid was decanted, concentrated to about one-tenth of its bulk, and treated with light petroleum so long as tar separated. The clear liquid was decanted, washed with dilute sodium hydroxide solution and with water, and dried over fused sodium sulphate. The sodium acetate and the tars were boiled with light petroleum, and the extract was worked up in the same manner as for the main yield. The 3-nitrodiphenyl crystallised from alcohol in pale yellow needles (yield, 10–12 g.), m. p. 62°.

*4'-Chloro-3-nitrodiphenyl* was prepared by passing dry chlorine into a mixture of 10 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 80°, until the gain in weight was 2 g.; or by passing chlorine into a 10% solution of 3-nitrodiphenyl in carbon tetrachloride in the presence of a trace of iodine and keeping the solution for several days. The product after repeated crystallisations from methyl alcohol separated in fine, white needles, m. p. 89° (Found: Cl, 14.9.  $C_{12}H_8O_2NCl$  requires Cl, 15.2%).

*4'-Chloro-3-acetamidodiphenyl*.—5 G. of 4'-chloro-3-nitrodiphenyl in 50 c.c. of alcohol were refluxed with 25 g. of stannous chloride in 25 c.c. of concentrated hydrochloric acid for 6 hours and the mixture was then cooled and rendered alkaline with 30% sodium hydroxide solution. The base, isolated by means of ether, was treated with excess of acetyl chloride in pyridine solution. The product crystallised from methyl alcohol in needles, m. p. 184° (Found: Cl, 14.6.  $C_{14}H_{12}ONCl$  requires Cl, 14.45%).

By the hydrolysis of the acetyl derivative with alcoholic hydrochloric acid 4'-chloro-3-aminodiphenyl was obtained. It separated from methyl alcohol in large needles, m. p. 82° (Found: Cl, 17.4).

$C_{12}H_{10}NCl$  requires Cl, 17.45%), and on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-chlorobenzoic acid (m. p. 240°).

2':4'-*Dichloro-3-nitrodiphenyl* was obtained when dry chlorine was led into a mixture of 5 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 100°, until the gain in weight was 2 g. The product was extracted with methyl alcohol and crystallised repeatedly from this solvent or from dilute acetic acid. It separated in needles, m. p. 115° (yield, 2—3 g.) (Found: Cl, 26.35.  $C_{12}H_7O_2NCl_2$  requires Cl, 26.5%).

On reduction of the dichloro-compound with alcoholic stannous chloride solution in the presence of a large amount of concentrated hydrochloric acid, extraction of the free base, and acetylation, 2':4':4'-*trichloro-3-acetamidodiphenyl* was obtained. It separated from dilute methyl alcohol in needles, m. p. 170° (Found: C, 53.6; H, 3.15.  $C_{14}H_{10}ONCl_3$  requires C, 53.4; H, 3.2%).

2':4':4'-*Trichloro-3-aminodiphenyl* was obtained on hydrolysis of the acetyl derivative. It separated from dilute methyl alcohol in needles, m. p. 105° (Found: Cl, 38.9.  $C_{12}H_8NCl_3$  requires Cl, 39.1%).

Oxidation of the base with chromic anhydride in glacial acetic acid solution yielded 2:4-dichlorobenzoic acid (m. p. 161°). The introduction of the chlorine atom into the molecule during the reduction of the nitro-compound would lead to a product substituted in the ring containing the amino-group (compare Blanksma, *Rec. trav. chim.*, 1906, 25, 365; Scarborough and Waters, this vol., p. 89); thus to the nitro-compound may be assigned the structure 2':4'-dichloro-3-nitrodiphenyl.

*Trichloro-3-nitrodiphenyl* was obtained together with mono- and di-chloro-derivatives when chlorine was passed into a mixture of 3-nitrodiphenyl and ferric chloride at 100° for some hours. The product was extracted with acetone and repeatedly crystallised from this solvent or from benzene. It separated in needles, m. p. 211°. The yield was less than 20% of the theoretical (Found: Cl, 35.2.  $C_{12}H_6O_2NCl_3$  requires Cl, 35.2%).

*Tetrachloro-3-nitrodiphenyl* was obtained when the chlorination was carried out at 120°. The product was extracted with acetone and recrystallised from this solvent repeatedly. It separated from alcohol as a matted mass of fine needles, m. p. 175° (Found: Cl, 42.5.  $C_{12}H_5O_2NCl_4$  requires Cl, 42.2%).

4'-*Bromo-3-nitrodiphenyl*.—5 G. of 3-nitrodiphenyl were ground into a paste with 0.5 g. of ferric chloride, and 7 g. of bromine added. After the mass had cooled, water was added and the whole heated on the water-bath for 30 minutes. The product separated from

alcohol in plates, m. p.  $95^{\circ}$  (yield, almost theoretical) (Found : Br, 28.85.  $C_{12}H_8O_2NBr$  requires Br, 28.8%).

4'-Bromo-3-aminodiphenyl was obtained on the reduction of the nitro-compound with stannous chloride in alcoholic hydrochloric acid solution. It separated from dilute alcohol in needles, m. p.  $105^{\circ}$  (Found : Br, 31.95.  $C_{12}H_{10}NBr$  requires Br, 32.2%).

On acetylation of the base in pyridine solution 4'-bromo-3-acetamidodiphenyl was obtained. It separated from alcohol in needles, m. p.  $193^{\circ}$  (Found : Br, 27.55.  $C_{14}H_{12}ONBr$  requires Br, 27.75%). The base on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-bromobenzoic acid (m. p.  $252^{\circ}$ ).

2 : 4 : 4' : 6-Tetrabromo-3-aminodiphenyl.—2 G. of the monobromo-base and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid. Excess of a 10% solution of bromine in acetic acid was added and the mixture gently warmed. The product, which separated on pouring into water, crystallised from alcohol in needles, m. p.  $104^{\circ}$  (Found : Br, 66.2.  $C_{12}H_7NBr_4$  requires Br, 66.0%). On oxidation, in glacial acetic acid solution, with chromic anhydride, bromine was liberated and *p*-bromobenzoic acid (m. p.  $251^{\circ}$ ) was isolated. Three bromine atoms must therefore be in the same ring as the amino-group, and the structure assigned depends partly on the direct bromination of 3-aminodiphenyl (see p. 3007).

3 : 4'-Dinitrodiphenyl.—A solution of 15 g. of 3-nitrodiphenyl in 250 c.c. of nitric acid (*d* 1.5) was kept over-night. The product, which separated when the mixture was poured into water, was digested with 500 c.c. of boiling methyl alcohol, the suspension allowed to cool, and the solid separated. It crystallised from acetone in pale yellow needles which melted, alone or mixed with the product of deamination of 3 : 4'-dinitro-4-aminodiphenyl (compare Scarborough and Waters, this vol., p. 1139), at  $189^{\circ}$ . Yield, 11–12 g.

2' : 3-Dinitrodiphenyl was obtained on evaporation of the methyl alcohol used for the digestion of the crude nitration product. It separated from dilute acetic acid in white plates, m. p.  $120^{\circ}$  (compare Cain, J., 1912, **101**, 2298). Yield, 5–6 g. (Found : N, 11.5. Calc. : N, 11.5%). The structure of the compound was determined in the following manner : 2' : 3-Dinitrobenzidine (Le Fèvre and Turner, J., 1926, 1759) was deaminated by grinding it to a paste with concentrated sulphuric acid, adding a little water and an excess of finely powdered sodium nitrite, followed by alcohol, and boiling the suspension under reflux for 30 minutes. The alcohol was partly removed and the dinitrodiphenyl separated. Crystallised from methyl alcohol and then from dilute acetic acid, it melted at  $119^{\circ}$ , alone or mixed with the product of direct nitration.

2' : 3 : 4 : 4'-*Tetranitrodiphenyl* was prepared by dissolving 2.5 g. of either 2' : 3- or 3 : 4'-dinitrodiphenyl in 60 c.c. of concentrated sulphuric acid and adding gradually 3 g. of finely ground potassium nitrate. The solution was kept over-night and then poured on crushed ice. The *tetranitro*-compound crystallised from methyl alcohol in pale yellow cubes, m. p. 173° (Found : C, 43.35; H, 1.8; N, 16.8.  $C_{12}H_6O_8N_4$  requires C, 43.1; H, 1.8; N, 16.75%). When it was warmed with an excess of piperidine for 5 minutes, and the solution poured into dilute hydrochloric acid, 2' : 3 : 4'-trinitro-4-piperidinodiphenyl separated; this crystallised from methyl alcohol in deep scarlet prisms, m. p. 143° (Found : C, 55.05; H, 4.4; N, 15.2. Calc. : C, 54.85; H, 4.3; N, 15.1%).

3-*Aminodiphenyl*.—A hot solution of 20 g. of 3-nitrodiphenyl in 200 c.c. of alcohol was added in portions to a solution of 120 g. of stannous chloride in 120 c.c. of hydrochloric acid, and the mixture refluxed for 4 hours. The tin double salt, which separated after removal of a part of the alcohol, was decomposed with 30% sodium hydroxide solution and the base was isolated by means of ether and distilled twice under diminished pressure (yield, 75%), b. p. 195°/15 mm., m. p. 30°.

3-Acetamidodiphenyl, prepared by refluxing a solution of the base in twice its weight of glacial acetic acid for 6 hours, separated from dilute alcohol in needles or small plates, m. p. 149°.

*N*-Chloro-3-acetamidodiphenyl.—10 G. of the acetyl derivative were suspended in a solution of 13 g. of sodium bicarbonate in 200 c.c. of water, and 150 c.c. of *N*-sodium hypochlorite added drop by drop with vigorous stirring. After 12 hours, the product was filtered off. It crystallised from light petroleum in masses of small needles, m. p. 87° (Found : available Cl, 14.1.  $C_{14}H_{12}ONCl$  requires Cl, 14.4%).

4-Chloro-3-acetamidodiphenyl.—(a) *Conversion of the chloroamine*. The chloroamine was dissolved in alcohol and a few c.c. of acetic acid were added; the solution was refluxed for 30 minutes. The product separated from dilute alcohol in plates, m. p. 148°.

(b) *Direct chlorination of 3-acetamidodiphenyl*. Chlorine diluted with carbon dioxide was passed into a 2% solution of the acetyl derivative in acetic acid and in the presence of fused sodium acetate. After the theoretical gain in weight had been obtained, the solution was kept for some hours and then poured into water. The product, precipitated as a gum, after repeated crystallisations from methyl alcohol, separated in plates, m. p. 148° (Found : Cl, 14.5.  $C_{14}H_{12}ONCl$  requires Cl, 14.4%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid 4-chloro-3-aminodiphenyl hydrochloride was obtained.

It separated from dilute hydrochloric acid in needles, m. p. 247° (decomp.) (Found: HCl, 15.45; total Cl, 29.4.  $C_{12}H_{10}NCl, HCl$  requires HCl, 15.2; Cl, 29.6%).

The decomposition of the salt with dilute aqueous ammonia gave a viscous oil which could not be obtained in a pure state. The salt was converted by the usual methods into 3:4-dichlorodiphenyl (m. p. 46°), and this compound on oxidation with chromic and acetic acids yielded 3:4-dichlorobenzoic acid (m. p. 198°).

*4-Bromo-3-acetamidodiphenyl.*—5 G. of 3-acetamidodiphenyl and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid and treated with 45 c.c. of a 10% solution of bromine in acetic acid. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from dilute alcohol in plates, m. p. 163° (Found: Br, 27.4.  $C_{14}H_{12}ONBr$  requires Br, 27.55%). On hydrolysis with 10% alcoholic hydrobromic acid, the base was obtained as a dark oil which decomposed on distillation under diminished pressure and separated as an oil from the usual solvents. The crude amine was converted, by the usual methods, into 3:4-dibromodiphenyl, a faintly yellow oil, b. p. 215°/15 mm. (Found: Br, 51.0.  $C_{12}H_8Br_2$  requires Br, 51.2%). On oxidation with chromic and acetic acids 3:4-dibromobenzoic acid was isolated (m. p. 228°).

*4:6-Dibromo-3-acetamidodiphenyl.*—A solution of 5 g. of 3-acetamidodiphenyl and 15 g. of sodium acetate in 100 c.c. of acetic acid was refluxed and treated with 12 g. of bromine in portions. The product, which separated as a gum when the mixture was poured into water, crystallised from methyl alcohol in needles, m. p. 149°. The yield was some 50% of the theoretical, the residue being a gum (Found: Br, 43.55.  $C_{14}H_{11}ONBr_2$  requires Br, 43.35%).

On hydrolysis of the acetyl derivative with alcoholic hydrobromic acid, the free base was obtained as a dark oil. This was converted into 2:4-dibromodiphenyl, a faintly yellow, viscid oil, b. p. 235°/15 mm. (Found: Br, 49.9.  $C_{12}H_8Br_2$  requires Br, 51.2%). On oxidation with chromic and acetic acids 2:4-dibromobenzoic acid (m. p. 169°) was isolated. The symmetry of the molecule prevents a definite proof of the 4:6-structure; but from steric considerations it is more probable than the 2:4-structure.

*4-Bromo-3-aminodiphenyl Hydrobromide.*—5 G. of 3-aminodiphenyl were dissolved in carbon tetrachloride and treated with 50 c.c. of a 10% solution of bromine in the same solvent. The precipitated hydrobromide was filtered off and triturated with a fresh quantity of bromine solution. It separated from dilute hydrobromic acid in needles, m. p. 255° (decomp.) (Found: Total Br, 49.0.



$C_{12}H_{10}NBr, HBr$  requires Br, 48.65%). The structure was determined by liberating the base with dilute aqueous ammonia and subsequent acetylation, 4-bromo-3-acetamidodiphenyl (m. p. 163°) being obtained.

2 : 4 : 6-*Tribromo-3-aminodiphenyl*.—(a) 5 G. of 4-bromo-3-aminodiphenyl were dissolved in 100 c.c. of carbon tetrachloride and treated with 3.5 g. of bromine. The product was separated, suspended in fresh carbon tetrachloride, and treated with 3 g. of bromine. The solid product crystallised from alcohol, containing a little ammonia, in small needles, m. p. 141°. (b) 5 G. of 3-aminodiphenyl and 20 g. of fused sodium acetate were dissolved in acetic acid and treated with 180 c.c. of a 10% solution of bromine in acetic acid. After 1 hour the product was precipitated by pouring the mixture into water (Found : Br, 58.85.  $C_{12}H_8NBr_3$  requires Br, 59.1%).

On oxidation of the base with chromic anhydride in glacial acetic acid solution, bromine was liberated and the molecule completely destroyed.

2 : 4 : 6-*Tribromodiphenyl* was obtained from the amine by the usual methods. It crystallised from methyl alcohol in needles, m. p. 64° (Found : Br, 61.7.  $C_{12}H_7Br_3$  requires Br, 61.4%). Since oxidation with chromic anhydride caused complete decomposition, no definite proof can be given that the third bromine atom enters the 2-position; from a comparison with the behaviour of 2 : 4 : 4' : 6-tetrabromo-3-aminodiphenyl, however, it may be reasonably assumed that all three bromine atoms are in one nucleus.

4-*Nitro-3-acetamidodiphenyl*.—A solution of 5 g. of 3-acetamidodiphenyl in a mixture of 30 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride was heated to 70°, a solution of 1.5 c.c. of nitric acid ( $d$  1.5) in 5 c.c. of acetic acid added drop by drop, and the temperature maintained for a further 30 minutes. The product, precipitated as a gum when the mixture was poured on ice, was extracted at once with alcohol, from which it separated in silky, pale yellow needles (yield, about 50%), m. p. 115° (Found : N, 11.1.  $C_{14}H_{12}O_3N_2$  requires N, 10.95%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid, 4-*nitro-3-aminodiphenyl* was obtained. It separated very slowly from dilute alcohol in orange needles, m. p. 116° (Found : N, 13.0.  $C_{12}H_{10}O_2N_2$  requires N, 13.1%). The base on deamination yielded 4-nitrodiphenyl (m. p. 114°).

4'-*Nitro-3-acetamidodiphenyl*.—5 G. of 3-acetamidodiphenyl were dissolved in 100 c.c. of nitric acid ( $d$  1.5) at 0°. After 15 minutes, the mixture was poured on ice, and the product, a gum, filtered off. After repeated crystallisations from alcohol, it separated in pale

yellow needles, m. p. 192° (yield, about 40%) (Found: N, 11.0.  $C_{14}H_{12}O_2N_2$  requires N, 10.95%).

The acetyl derivative on hydrolysis yielded 4'-nitro-3-aminodiphenyl, which separated from alcohol in long, orange needles, m. p. 137° (Found: N, 12.95.  $C_{12}H_{10}O_2N_2$  requires N, 13.1%), and on oxidation with chromic and acetic acids yielded *p*-nitrobenzoic acid (m. p. 238°).

4-Bromo-4'-nitro-3-acetamidodiphenyl.—A solution of 5 g. of 4-bromo-3-acetamidodiphenyl in 100 c.c. of nitric acid (*d* 1.5) was kept for 20 minutes and then poured on ice. The product was immediately extracted with methyl alcohol, from which it separated slowly, on dilution, in yellow needles, m. p. 158° (yield, about 40%) (Found: N, 8.4.  $C_{14}H_{11}O_3N_2Br$  requires N, 8.35%).

By the hydrolysis of this acetyl derivative with 10% alcoholic hydrochloric acid, 4-bromo-4'-nitro-3-aminodiphenyl was obtained. It separated from dilute methyl alcohol in red needles, m. p. 145° (Found: N, 9.7.  $C_{12}H_9O_2N_2Br$  requires N, 9.55%). The base on oxidation with chromic anhydride yielded *p*-nitrobenzoic acid (m. p. 238°).

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