2. *A New Reaction of Certain Diazosulphonates derived from β-Naphthol-*1*-sulphonic Acid. Part VIII. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from* 2*-Chloro-*4*-nitroaniline.*

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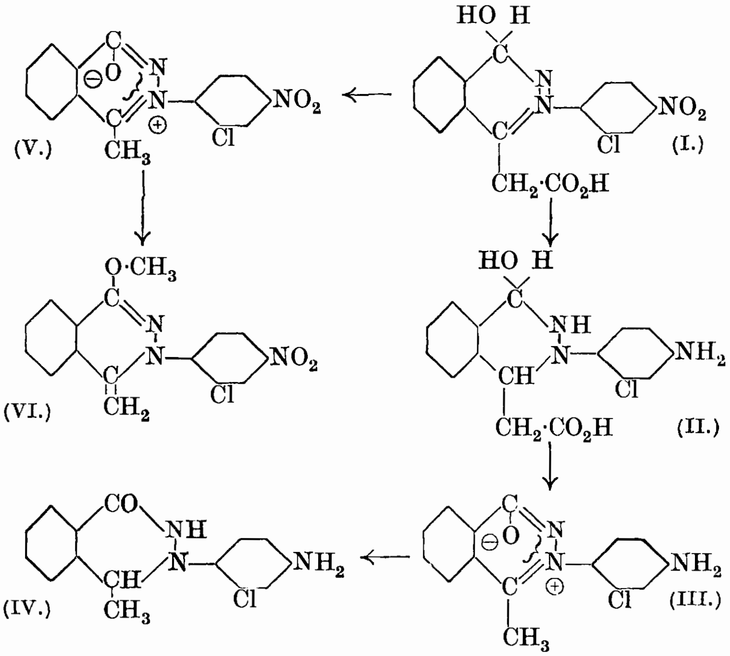
In Part VI (J., 1931, 1073), the preparation of phthalazine, phthalazone, and phthalimidine derivatives from 2′ : 6′-dichloro-4′-nitrobenzene-2-naphthol-1-diazosulphonate has been described. In certain instances the results were different from those obtained in the absence of the chlorine atoms (J., 1926, 690; 1928, 2550; 1931, 1067) and further evidence in support of the constitutions attributed to some of the compounds was desirable. Consequently, the corresponding 2′-chloro-4′-nitro- and -amino-derivatives were investigated.

In general, the yields and properties of the present series of compounds are intermediate between those of the corresponding 2′ : 6′-dichloro- and unchlorinated compounds, although there are some exceptions. Many of the 2′ : 6′-dichloro-derivatives were found to be associated with organic solvent of crystallisation, and this feature is again noteworthy.

1-Hydroxy-3-(2′ : 6′-dichloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid is best reduced to 1-hydroxy-3-(2′ : 6′-dichloro-4′-aminophenyl)tetrahydrophthalazine-4-acetic acid by stannous chloride and hydrochloric acid, whereas in the absence of the chlorine atoms this reduction is best effected by alkaline hydrosulphite (hyposulphite), and the latter is also the case with the 2′-*chloro*-compound (I ⟶ II), because subsequent degradation occurs more readily with acid than with alkali.

A compound intermediate between an amino-3-phenylphthalaz-1-one and an amino-*N*-phenylphthalimidine has only been obtained with certainty as yet in the case of 3′-amino-3-phenyl-4-methylphthalaz-1-one, which gave 1-keto-3-(3′-aminophenyl)-4-methyltetrahydrophthalazine (J., 1931, 1919). Both 2′-*chloro*-4′-*amino*-3-*phenylphthalaz*-1-*one* and its 4-*methyl* derivative (III), however, under suitable conditions are reduced to 1-*keto*-3-(2′-*chloro*-4′-*aminophenyl*)*tetrahydrophthalazine* and its 4-*methyl* derivative (IV) respectively. Moreover, the stability of these intermediate compounds renders their conversion into 2′-*chloro*-4′-*amino*-N-*phenyl*-



phthalimidine and its 3-*methyl* derivative respectively extremely difficult and the yields of the latter are low. In all examples previously recorded, nitro-3-phenylphthalaz-1-ones are merely reduced by aqueous sodium sulphide to the corresponding amino-derivatives, and although this is also the case with 2′-*chloro*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one* when reduction is rapid, prolonged boiling gives 1-keto-3-(2′-chloro-4′-aminophenyl)-4-methyltetrahydrophthalazine.

The compounds obtained by methylating the oxygen atom in the keto-group of 4′-nitro-3-phenylphthalaz-1-one and its 2′ : 6′-dichloro-derivative possess entirely different properties (J., 1931, 1075). It was anticipated that further information in this connection might be obtained from 2′-chloro-4′-nitro-3-phenylphthalaz-1-one. Remarkable difficulties were encountered in preparing this compound, however, and although formed, it could not be purified. The impure substance was methylated, but the product also resisted all attempts to purify it. On the other hand, 2′-*chloro*-4′-*nitro*-3-*phenyl*-4-*methylphthalaz*-1-*one* (V) is obtained in a normal manner, and methyl sulphate, followed by treatment with alkali, undoubtedly converts it into 2′-*chloro*-4′-*nitro*-1-*methoxy*-3-*phenyl*-4-*methylene*-3 : 4-*dihydrophthalazine* (VI).

EXPERIMENTAL.

Where no details of preparation are given, the 2′-chloro-compounds were prepared exactly as described for the corresponding 2′ : 6′-dichloro-compounds (J., 1931, 1078).

Sodium Hydrogen 3-(2′-*Chloro*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*.—A filtered solution of 50 g. of commercial 50% sodium β-naphthol-1-sulphonate in 120 c.c. of water was stirred at 0° into a solution of diazotised 2-chloro-4-nitroaniline. The latter was obtained by boiling 17 g. of 2-chloro-4-nitroaniline with 180 c.c. of concentrated hydrochloric acid and 100 c.c. of water until dissolved, then adding 80 g. of ice with stirring and external cooling so that the hydrochloride separated in a fine condition, and finally adding a concentrated aqueous solution of 7·5 g. of sodium nitrite. The diazo-solution was filtered from unaltered base (1 g.). The 2′-chloro-4′-nitrobenzene-2-naphthol-1-diazosulphonate separated immediately as an orange-brown precipitate, which was treated successively with sodium carbonate and hydroxide solutions. Orange needles of sodium 1-(2′-chloro-4′-nitrobenzeneazo)-β-naphthaquinone-1-sulphonate separated from the sodium carbonate solution, and 2′-chloro-4′-nitrobenzeneazo-β-naphthol (2—3 g.) was removed after acidification of the sodium hydroxide solution. *Sodium hydrogen* 3-(2′-*chloro*-4′-*nitrophenyl*)-1 : 3-*dihydro*-

phthalazine-1-*sulphonate*-4-*acetate* (yield, 34·5 g.; 83%, calculated on the 2-chloro-4-nitroaniline actually diazotised) crystallised from water (charcoal) or from ethyl acetate in small yellow needles (Found: S, 7·3; Cl, 7·8. $C_{16}H_{11}O_7N_3ClSNa$ requires S, 7·15; Cl, 7·9%). It was readily soluble in water or alcohol, but less soluble in ethyl acetate. The greenish-yellow aqueous solution was deepened in colour by the addition of alkalis, and was decolorised by zinc dust and ammonia, a deeper colour returning on exposure to air. It is a yellow acid dye intermediate in tinctorial power between the corresponding unhalogenated compound and the 2′ : 6′-dichloro-compound, and fugitive to light.

1-*Hydroxy*-3-(2′-*chloro*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid* (I).—This was prepared from the preceding sodium hydrogen salt (20 g.). It crystallised (*a*) from toluene in faintly yellow, prismatic needles, m. p. 110—130°, containing ¼ mol. toluene of crystallisation, removed at 150°; it then melted at 204° (Found: loss at 150°, 5·5. $C_{16}H_{12}O_5N_3Cl,\frac{1}{4}C_7H_8$ requires C_7H_8, 5·9%), (*b*) from ethyl acetate in greenish-yellow prisms, m. p. 204° (yield, 14·5 g.; 89·7%) (Found: C, 53·2; H, 3·2; N, 11·6; Cl, 9·7. $C_{16}H_{12}O_5N_3Cl$ requires C, 53·1; H, 3·3; N, 11·6; Cl, 9·8%). It was readily soluble in alcohol, acetone, or glacial acetic acid, but very sparingly soluble in ether. It was sparingly soluble in water, forming a solution acid to litmus, but dissolved readily in sodium carbonate or hydroxide with a deep orange-red colour. It dissolved in cold concentrated sulphuric acid with an orange colour and was reprecipitated unaltered on dilution, but when it was boiled with aqueous sulphuric acid 2′-chloro-4′-nitro-3-phenylphthalaz-1-one was formed (p. 17).

Derivatives of 1-*Hydroxy*-3-(2′-*chloro*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—The *methyl* ester crystallised from benzene in yellow prismatic needles, softening at 120° and melting at 135—145°, containing ½ mol. benzene of crystallisation, or m. p. 166° after removal of the benzene (Found: loss at 120°, 9·5. $C_{17}H_{14}O_5N_3Cl,\frac{1}{2}C_6H_6$ requires C_6H_6, 9·4%. Found in material dried at 120°: C, 54·5; H, 3·6. $C_{17}H_{14}O_5N_3Cl$ requires C, 54·3; H, 3·7%). The *ethyl* ester crystallised from benzene in small, pale yellow needles, softening at 100° and melting at 168°, containing ½ mol. benzene of crystallisation, partly lost at air temperature and removed completely at 120°; it then melted at 169° (Found: loss at 120°, 8·5. $C_{18}H_{16}O_5N_3Cl,\frac{1}{2}C_6H_6$ requires C_6H_6, 9·1%. Found in material dried at 120°: C, 55·4; H, 4·2. $C_{18}H_{16}O_5N_3Cl$ requires C, 55·5; H, 4·1%). The *acetyl* derivative crystallised from ethyl alcohol (charcoal) in yellow prismatic needles, softening at 110° and melting at 118°, containing ½ mol. ethyl alcohol of crystallisation, removed at 110°; it then melted at 153° (Found: loss at 110°, 5·6. $C_{18}H_{14}O_6N_3Cl,\frac{1}{2}C_2H_6O$ requires C_2H_6O, 5·6%. Found in material dried at 110°: C, 53·7; H, 3·7. $C_{18}H_{14}O_6N_3Cl$ requires C, 53·5; H, 3·5%). It dissolved in sodium carbonate with an orange-brown colour and in sodium hydroxide with a brownish-red colour. The *anilide* crystallised from alcohol in yellow prisms, m. p. 195° (Found: C, 60·3; H, 4·0; Cl, 7·9. $C_{22}H_{17}O_4N_4Cl$ requires C, 60·5; H, 3·9; Cl, 8·1%). It was sparingly soluble in warm sodium hydroxide solution with a brownish-red colour.

1-*Hydroxy*-3-(2′-*chloro*-4′-*aminophenyl*)*tetrahydrophthalazine*-4-*acetic Acid* (II).—(*a*) Hydrosulphite was added to a solution of 20 g. of 1-hydroxy-3-(2′-chloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 250 c.c. of water and 18 g. of sodium hydroxide at about 90° until the deep red colour had disappeared, the mixture being kept alkaline throughout by the addition of sodium hydroxide. The solution was cooled quickly to limit the action of the alkali on the product, filtered from a little 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one (p. 18), and hydrochloric acid added to the filtrate until a white precipitate had separated completely. This, after being washed with cold water, crystallised from ethyl acetate in almost colourless prisms, m. p. 236—237° (decomp.) (yield, 17·2 g.; 93%) (Found: C, 57·3; H, 4·6; N, 12·5; Cl, 10·7. $C_{16}H_{16}O_3N_3Cl$ requires C, 57·6; H, 4·8; N, 12·6; Cl, 10·6%), insoluble in ether or benzene, but soluble in acetone or alcohol. It was sparingly soluble in water, but was readily soluble in dilute acids and alkalis, and could be diazotised. (*b*) A mixture of 24 g. of finely powdered 1-hydroxy-3-(2′-chloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid with a solution of 96 g. of stannous chloride in 240 c.c. of concentrated hydrochloric acid was boiled until the pale yellow compound dissolved. After cooling, the colourless solution was rendered alkaline with sodium hydroxide, filtered, the precipitate washed with sodium carbonate, and dilute hydrochloric acid added to the united filtrate and washings until a white precipitate had separated completely. This crystallised from ethyl acetate in colourless prisms, m. p. 236—237° (yield, 16·8 g.; 76%). The *acetyl* derivative crystallised from alcohol in almost colourless needles, m. p. 277° (Found: C, 57·4; H, 4·6. $C_{18}H_{18}O_4N_3Cl$ requires C, 57·5; H, 4·8%).

2′-*Chloro*-4′-*amino*-3-*phenylphthalaz*-1-*one*.—This was prepared from 1-hydroxy-3-(2′-chloro-4′-aminophenyl)tetrahydrophthalazine-4-acetic acid (10 g.). The diluted acid filtrate was rendered alkaline with sodium carbonate; the precipitate obtained crystallised from alcohol in small yellow needles, m. p. 240° (decomp.) (yield, 5·9 g.; 72·5%) (Found: C, 61·7; H, 3·9; Cl, 12·9. $C_{14}H_{10}ON_3Cl$ requires

C, 61·9; H, 3·7; Cl, 13·1%), readily soluble in mineral acids (the hydrochloride is soluble in cold concentrated hydrochloric acid) and soluble in hot sodium hydroxide solution with a yellow colour. 2′-Chloro-4′-amino-3-phenylphthalaz-1-one was prepared also (yield, 69%) by boiling a solution of 1-hydroxy-3-(2′-chloro-4′-aminophenyl)tetrahydrophthalazine-4-acetic acid in excess of concentrated hydrochloric acid under reflux for 20 hours (compare J., 1926, 703). The *acetyl* derivative crystallised from alcohol in small colourless prismatic needles, darkening at 290° and melting at 321° (decomp.) (Found: C, 61·4; H, 4·0; Cl, 11·2. $C_{16}H_{12}O_2N_3Cl$ requires C, 61·2; H, 3·8; Cl, 11·3%).

1-*Keto*-3-(2′-*chloro*-4′-*aminophenyl*)*tetrahydrophthalazine*.—A fine suspension of 2′-chloro-4′-amino-3-phenylphthalaz-1-one, obtained by adding a solution of 2 g. in 2 c.c. of concentrated hydrochloric acid and 40 c.c. of water to a solution of 4 g. of sodium hydroxide in 40 c.c. of water, was kept just below the boiling point and excess sodium hydrosulphite added, the mixture being kept alkaline with sodium hydroxide. After ¼ hour, the mixture was cooled, and the white precipitate removed; it crystallised from alcohol in almost colourless prisms, m. p. 220—223° (yield, 1·3 g.; 64·5%) (Found: C, 61·8; H, 4·4; N, 15·6; Cl, 12·7. $C_{14}H_{12}ON_3Cl$ requires C, 61·4; H, 4·4; N, 15·4; Cl, 13·0%). The hydrochloride is insoluble in cold concentrated hydrochloric acid. The *acetyl* derivative crystallised from alcohol in colourless prisms, m. p. 217—219° (Found: N, 13·5. $C_{16}H_{14}O_2N_3Cl$ requires N, 13·3%), readily hydrolysed to the base by boiling hydrochloric acid.

2′-*Chloro*-4′-*amino*-N-*phenylphthalimidine*.—A solution of 5 g. of 2′-chloro-4′-amino-3-phenylphthalaz-1-one in 400 c.c. of water and 20 c.c. of concentrated hydrochloric acid was boiled vigorously while 8 g. of zinc dust and a further 40 c.c. of concentrated hydrochloric acid were added in small portions during 1½ hours. After cooling, the solution was almost neutralised with sodium hydroxide, and the white precipitate (3·2 g.) filtered off. The product contained 1-keto-3-(2′-chloro-4′-aminophenyl)tetrahydrophthalazine, which was removed by repeated fractional crystallisation from alcohol, in which it is less soluble. 2′-*Chloro*-4′-*amino*-N-*phenylphthalimidine* crystallised from ethyl alcohol in colourless rhombohedra, m. p. 188—189°, containing ¼ mol. ethyl alcohol of crystallisation, which was difficult to remove completely (Found: loss at 150°, 3·8. $C_{14}H_{11}ON_2Cl,\frac{1}{4}C_2H_6O$ requires C_2H_6O, 4·2%. Found in material dried at 150°: C, 65·3; H, 4·6; Cl, 13·8. $C_{14}H_{11}ON_2Cl$ requires C, 65·0; H, 4·3; Cl, 13·7%). The *acetyl* derivative crystallised from alcohol in small colourless needles, m. p. 234° (Found: C, 63·8; H, 4·1. $C_{16}H_{13}O_2N_2Cl$ requires C, 63·9; H, 4·3%).

2′-Chloro-4′-nitro-3-phenylphthalaz-1-one.—A solution of 10 g. of 1-hydroxy-3-(2′-chloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 40 c.c. of concentrated sulphuric acid was diluted with 18 c.c. of water, the formation of any precipitate being avoided, as this was difficult to redissolve subsequently. The clear solution was kept at 130° under reflux, 30 c.c. of water were added gradually with vigorous shaking, and the whole was boiled for 2 hours. The solution was cooled, diluted with 100 c.c. of water, boiled for ½ hour (charcoal), and filtered. After cooling, no sulphate separated (compare J., 1928, 2553; 1931, 1084) and the cold yellow solution was neutralised with sodium carbonate. The yellow precipitate (4·4 g.), m. p. 130—150°, could not be crystallised from organic solvents, resins only being obtained. It undoubtedly consisted of impure 2′-chloro-4′-nitro-3-phenylphthalaz-1-one, as reduction with aqueous sodium sulphide gave one-fifth of its weight of 2′-chloro-4′-amino-3-phenylphthalaz-1-one (p. 15), m. p. and mixed m. p. 240°.

Action of methyl sulphate. With methyl sulphate in dry nitrobenzene at 110°, the crude nitro-compound gave, after removal of the nitrobenzene, a yellow aqueous residue, from which a brownish-yellow precipitate was obtained when rendered alkaline with sodium carbonate. This basic substance resisted all attempts to crystallise it from organic solvents, and melted at 154° (decomp.), with previous shrinking and darkening at 125—130° (Found : N, 13·4; OMe, 9·0, 9·2%).

2′-Chloro-4′-nitro-3-phenyl-4-methylphthalaz-1-one (V).—A solution of 10 g. of finely powdered 1-hydroxy-3-(2′-chloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 90 c.c. of cold concentrated sulphuric acid was poured on 240 g. of ice, and 4·6 g. of powdered potassium dichromate were added in small portions during 2 hours, with constant agitation. After 5 hours, the green solution was filtered and almost neutralised with concentrated aqueous sodium hydroxide (with ice cooling) and the pale yellow precipitate produced was washed with water and dried. *2′-Chloro-4′-nitro-3-phenyl-4-methylphthalaz-1-one* crystallised from alcohol or glacial acetic acid in pale yellow, prismatic needles, m. p. 201° (yield, 5·8 g.; 66·4%) (Found : C, 57·3; H, 3·5; N, 13·4; Cl, 11·0. $C_{15}H_{10}O_3N_3Cl$ requires C, 57·1; H, 3·2; N, 13·3; Cl, 11·3%). It was soluble in mineral acids and dissolved in sodium hydroxide with an orange-red colour. With an alcoholic solution of picric acid, after boiling for some time, it forms a *picrate*, brownish-yellow prisms, m. p. 204—205° (Found : C, 46·6; H, 2·65. $C_{21}H_{13}O_{10}N_6Cl$ requires C, 46·3; H, 2·4%).

Action of methyl sulphate. A solution of 3 g. of 2′-chloro-4′-

nitro-3-phenyl-4-methylphthalaz-1-one in 100 c.c. of hot dry nitrobenzene was treated with 1·6 g. of methyl sulphate as described for the corresponding unhalogenated compound (J., 1931, 1071), but the temperature was kept at 100° for ¾ hour. The basic product was *2′-chloro-4′-nitro-1-methoxy-3-phenyl-4-methylene-3 : 4-dihydrophthalazine* (VI), which crystallised from ethyl acetate in dark brownish-red prisms, m. p. 133° (yield, 1·3 g.; 41·5%) (Found: C, 58·4; H, 3·5; OMe, 9·7. $C_{16}H_{12}O_3N_3Cl$ requires C, 58·3; H, 3·6; OMe, 9·4%). It was very soluble in mineral acids, forming colourless solutions from which it was recovered unaltered on neutralisation.

2′-Chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one (III).—(*a*) A solution of 10 g. of 1-hydroxy-3-(2′-chloro-4′-aminophenyl)tetrahydrophthalazine-4-acetic acid in 25 c.c. of cold concentrated sulphuric acid was poured on 100 g. of ice and 3 g. of powdered potassium dichromate were added in portions during 1 hour, with constant agitation. Next day, the green solution was filtered, the filtrate neutralised with sodium carbonate, and the brown precipitate filtered off. The product was dissolved in boiling dilute hydrochloric acid (charcoal), and the warm filtered solution rendered alkaline. *2′-Chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one* crystallised from alcohol in pale yellow needles, m. p. 285° (yield, 7·2 g.; 84%) (Found: C, 63·2; H, 4·4; N, 14·8; Cl, 12·6. $C_{15}H_{12}ON_3Cl$ requires C, 63·1; H, 4·2; N, 14·7; Cl, 12·4%), insoluble in benzene or ether. It forms a hydrochloride, colourless needles, soluble in cold concentrated hydrochloric acid. (*b*) A solution of 10 g. of 1-hydroxy-3-(2′-chloro-4′-aminophenyl)tetrahydrophthalazine-4-acetic acid in 100 c.c. of water and 10 g. of sodium hydroxide was heated under reflux at about 90° for several days; the product separated progressively in yellow needles and was filtered off at intervals, the yield being 4·8 g., *i.e.*, 56%, after recrystallisation from alcohol. (*c*) Reduction of 2′-chloro-4′-nitro-3-phenyl-4-methylphthalaz-1-one with aqueous sodium sulphide as described for the corresponding unhalogenated compound (*loc. cit.*, p. 1072) also gave 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one (yield, 60%), but by continuing boiling for 3 hours a colourless crystalline precipitate of 1-keto-3-(2′-chloro-4′-aminophenyl)-4-methyltetrahydrophthalazine separated.

The *acetyl* derivative of 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one crystallised from dilute acetic acid in almost colourless prisms, m. p. 308° (decomp.), which darken on keeping (Found: C, 62·4; H, 4·5; N, 12·7; Cl, 11·0. $C_{17}H_{14}O_2N_3Cl$ requires C, 62·3; H, 4·3; N, 12·8; Cl, 10·8%).

1-Keto-3-(2′-chloro-4′-aminophenyl)-4-methyltetrahydrophthalazine

(IV).—(*a*) A fine suspension of 4 g. of 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one, obtained as described for the corresponding unmethylated compound (p. 15), was reduced with excess of sodium hydrosulphite under similar conditions. 1-*Keto*-3-(2′-*chloro*-4′-*aminophenyl*)-4-*methyltetrahydrophthalazine* crystallised from toluene in straw-coloured prismatic needles, m. p. 220—223° (yield, 3·2 g.; 79·4%) (Found: C, 62·9; H, 4·9; N, 15·0; Cl, 12·2. $C_{15}H_{14}ON_3Cl$ requires C, 62·6; H, 4·9; N, 14·6; Cl, 12·3%), soluble in alcohol. The hydrochloride, colourless needles, is insoluble in cold concentrated hydrochloric acid. On prolonged boiling with hydrochloric acid, it was partially oxidised to 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one.

(*b*) A solution of 2 g. of 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one in 50 c.c. of dilute hydrochloric acid (1 : 4) was boiled, and 3 g. of zinc dust added in small portions during 10 minutes. The solution was then filtered, neutralised with sodium hydroxide, the dried precipitate extracted with toluene, and the toluene distilled (yield, 1 g.; 49·6%). The *acetyl* derivative crystallised from toluene in colourless prisms, m. p. 218—220° (Found: C, 61·9; H, 4·7; N, 12·6; Cl, 10·6. $C_{17}H_{16}O_2N_3Cl$ requires C, 61·9; H, 4·9; N, 12·75; Cl, 10·8%).

2′-*Chloro*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine*.—A solution of 4 g. of 2′-chloro-4′-amino-3-phenyl-4-methylphthalaz-1-one in 100 c.c. of dilute hydrochloric acid (1 : 10) was boiled while 30 g. of zinc dust were added in small portions during 6 hours, the volume being kept constant by the addition of dilute hydrochloric acid. After cooling, the solution was rendered strongly alkaline with sodium hydroxide, and filtered, the dry precipitate extracted with alcohol, and the alcohol distilled. 2′-*Chloro*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine* crystallised from alcohol in colourless prismatic needles, m. p. 212° (yield, 1·2 g.; 31·4%) (Found: C, 66·3; H, 4·7; N, 10·5; Cl, 13·1. $C_{15}H_{13}ON_2Cl$ requires C, 66·1; H, 4·8; N, 10·3; Cl, 13·0%). The *acetyl* derivative crystallised from alcohol in colourless prisms, m. p. 253° (Found: C, 65·1; H, 4·6. $C_{17}H_{15}O_2N_2Cl$ requires C, 64·9; H, 4·8%).

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