CXXXVIII.—*A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part VI. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from 2 : 6-Dichloro- and 2 : 6-Dibromo-4-nitroaniline.**

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In Parts I, II, III, and V of this series (J., 1926, 690; 1928, 2550, 2556; preceding paper), the preparation of phthalazine, phthalazone, and phthalimidine derivatives from 4′- and 3′-nitrobenzene-2-naphthol-1-diazosulphonate has been described. The investigation has now been extended to the corresponding 2′ : 6′-dichloro- and 2′: 6′-dibromo-4′-nitro- and -amino-derivatives.

2′ : 6′-Dichloro- and 2′ : 6′-dibromo-4′-nitrobenzene-2-naphthol-1-diazosulphonate are formed readily from the diazotised 2 : 6-dihalogeno-4-nitroanilines and β-naphthol-1-sulphonic acid in acid solution, but conversion through the sodium 1-(2′ : 6′-dihalogeno-4′-nitrobenzeneazo)-β-naphthaquinone-1-sulphonates into the *sodium hydrogen* 3-(2′ : 6′-*dihalogeno*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-

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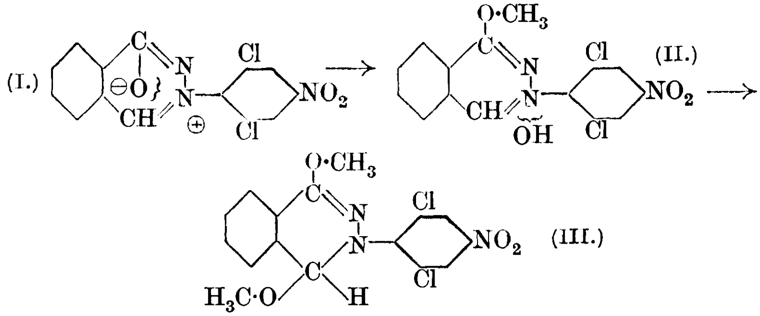
* The work on the dichloro-compounds was done with Mr. Dunbar, and that on the dibromo-compounds with Mr. Williams.

1-*sulphonate*-4-*acetates* does not proceed so readily (yield of the dichloro-compound, 16% less) as in the case of the unhalogenated analogue, owing to an increased tendency to the formation of 2′ : 6′-dihalogeno-4′-nitrobenzeneazo-β-naphthols. The conversion of the dibromo-compound proceeds less readily than that of the dichloro-compound. The sodium hydrogen salts resemble the corresponding unhalogenated compound (J., 1926, 699) in general properties, although possessing much less tinctorial power, particularly in the case of the dibromo-compound. The main influence of the presence of the halogen atoms usually is to render some of the subsequent stages of degradation rather more difficult to carry out and diminish the yields of the derivatives somewhat. The replacement of the sodium-1-sulphonate group by hydroxyl gives the 1-*hydroxy*-3-(2′ : 6′-*dihalogeno*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acids*, and *esters* and an *anilide* of each of these were obtained readily, the presence of solvent of crystallisation in many of the derivatives being noteworthy. The dichloro-compound also gave an *acetyl* derivative, but not the dibromo-compound, which in this respect resembles the 3′-nitro-analogue (J., 1928, 2556). Unlike the 4′-nitro-analogue, the 3′-nitro-analogue is not reduced to the aminotetrahydrophthalazine derivative satisfactorily by alkaline hydrosulphite (hyposulphite) owing to the subsequent action of alkali (*loc. cit.*). The 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acids also are not reduced satisfactorily by alkaline hydrosulphite, the reason for this being explained later. The 1-*hydroxy*-3-(2′ : 6′-*dihalogeno*-4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic acids* are obtained satisfactorily, however, by reduction with stannous chloride and hydrochloric acid, because the hydrochlorides are so sparingly soluble in concentrated hydrochloric acid that the reaction does not proceed further even after prolonged boiling. On the other hand, by boiling the 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acids with dilute sulphuric acid (b. p. 140°), acetic acid is eliminated and the 2′ : 6′-*dihalogeno*-4′-*amino*-3-*phenylphthalaz*-1-*ones* are obtained. When 2′ : 6′-dichloro-4′-amino-3-phenylphthalaz-1-one is reduced with zinc dust and hydrochloric acid, one nitrogen atom is eliminated as ammonia and 2′ : 6′-*dichloro*-4′-*amino*-N-*phenylphthalimidine* is produced. This reaction does not proceed so readily (yield, 24% less) as in the absence of the chlorine atoms (*loc. cit.*), owing to an increased tendency to fission with formation of 2 : 6-dichloro-*p*-phenylenediamine. There was, however, no evidence of the elimination of chlorine during this reaction. 2′ : 6′-*Dichloro*-N-*phenylphthalimidine* is formed readily by the replacement of the amino-group by hydrogen.

When 2′ : 6′-dibromo-4′-amino-3-phenylphthalaz-1-one is reduced with zinc dust and hydrochloric acid, bromine is eliminated and 4′-amino-*N*-phenylphthalimidine is the main product. By varying the conditions and limiting the reaction, some *2′-bromo-4′-amino-N-phenylphthalimidine* was formed, but the elimination of bromine could not be prevented entirely and no trace of the 2′ : 6′-dibromo-derivative was detected. This elimination of bromine is of interest, because a similar reduction of 2 : 6-dibromo-4-nitroaniline gives solely 2 : 6-dibromo-*p*-phenylenediamine.

When the 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acids are boiled with sulphuric acid (b. p. 140°), they lose acetic acid and the *2′ : 6′-dihalogeno-4′-nitro-3-phenylphthalaz-1-ones* are formed. These compounds are acidic and dissolve in sodium hydroxide solution with a bluish-red colour; also they are basic and dissolve in mineral acids, forming well-crystallised salts, decomposed by water; and they form *picrates*. The products obtained from them by reduction vary with the conditions used: reduction with aqueous sodium sulphide gives the 2′ : 6′-dihalogeno-4′-amino-3-phenylphthalaz-1-ones [the yield from the dichloro-compound was 36% less than that obtained by the action of aqueous sulphuric acid on 1-hydroxy-3-(2′ : 6′-dichloro-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid], whereas reduction with zinc dust and hydrochloric acid produces 2′ : 6′-dichloro-4′-amino-*N*-phenylphthalimidine from the dichloro-compound, and 4′-amino-*N*-phenylphthalimidine from the dibromo-compound.

The 2′ : 6′-dihalogeno-4′-nitro-3-phenylphthalaz-1-ones react with methyl sulphate in a similar manner to the 4′-nitro-analogue, and the primary products behave similarly with alcohols (*loc. cit.*). Thus, the interaction of 2′ : 6′-dichloro-4′-nitro-3-phenylphthalaz-1-one (I) with methyl sulphate in nitrobenzene solution, after removal of the latter, gives an aqueous solution of the methosulphate, from which a base (probably II) is isolated as an orange-yellow powder by means of sodium carbonate. This *substance* crystallises from ethyl acetate in orange plates, m. p. 235°, from methyl alcohol in orange prisms, m. p. 157°, and from ethyl alcohol in orange prisms, m. p. 111°. The corresponding dibromo-base crystallises from ethyl acetate in orange-yellow plates, m. p. 228°, from methyl alcohol in orange prisms, m. p. 138°, and from ethyl alcohol in orange prisms, m. p. 110—112°. Combination with the alcohols has occurred in both cases, but a portion is lost so readily from the dichloro-compound that the formula cannot be determined by analysis; this, however, indicates the presence of two alkyloxy-groups, and the formula (III) is supported by analysis of the corresponding dibromo-derivative, which loses alcohol only slowly on keeping. Unlike the behaviour of the corresponding substances from 4′- or



3′-nitro-3-phenylphthalaz-1-one (*loc. cit.*), however, heating first at 110° and then at 140° does not give the 4-keto-1-methoxy-3-(2′ : 6′-dihalogeno-4′-nitrophenyl)-3 : 4-dihydrophthalazines, but merely removes alcohol and gives the monomethoxy-compounds, m. p. 235° (dichloro-) and 228° (dibromo-), identical with those originally obtained by crystallisation from ethyl acetate. The latter substances require further investigation: the dichloro-compound does not appear to be (II), but is probably formed from it by a reaction involving the elimination of water.

The 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acids are decarboxylated by cold acid dichromate and the 2′ : 6′-*dihalogeno*-4′-*nitro*-3-*phenyl*-4-*methylphthalaz*-1-*ones* are formed. The yield of the dibromo-compound is 37% less than that of the dichloro-compound, which is 15% greater than that obtained in the absence of the chlorine atoms, and the substance is purified much more readily. These two compounds are acidic and dissolve in sodium hydroxide with a bluish-red colour; also they are basic and dissolve in moderately concentrated mineral acids; and they form *picrates*.

1-Hydroxy-3-(2′ : 6′-dichloro-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid also is decarboxylated by cold acid dichromate and 2′ : 6′-*dichloro*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one* is formed. The same substance is obtained in almost equally good yield by heating the acid with 10% aqueous sodium hydroxide at 90°, which explains the difficulty mentioned earlier of preparing the acid satisfactorily by the use of alkaline hydrosulphite. It is obtained also by reducing 2′ : 6′-dichloro-4′-nitro-3-phenyl-4-methylphthalaz-1-one with aqueous sodium sulphide.

2′ : 6′-*Dibromo*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one* is obtained much more readily than the corresponding dichloro-compound by the action of cold acid dichromate or aqueous permanganate on 1-hydroxy-3-(2′ : 6′-dibromo-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid, and the same substance is formed by boiling the latter with aqueous sodium carbonate, or by reducing 2′ : 6′-dibromo-4′-nitro-3-phenyl-4-methylphthalaz-1-one with aqueous sodium sulphide.

There is no difficulty in preparing 4′-amino-*N*-phenyl-3-methylphthalimidine by reducing 4′-amino-3-phenyl-4-methylphthalaz-1-one with zinc dust and hydrochloric acid, and no great difficulty in preparing 2′ : 6′-dichloro-4′-amino-*N*-phenylphthalimidine similarly from 2′ : 6′-dichloro-4′-amino-3-phenylphthalaz-1-one. Attempts to prepare 2′ : 6′-dichloro-4′-amino-*N*-phenyl-3-methylphthalimidine in this way from 2′ : 6′-dichloro-4′-amino-3-phenyl-4-methylphthalaz-1-one, however, were unsuccessful, the only reaction product which could be isolated being 2 : 6-dichloro-*p*-phenylenediamine, although a variety of conditions was employed. There were indications of the existence of the intermediate 1-keto-3-(2′ : 6′-dichloro-4′-aminophenyl)-4-methyltetrahydrophthalazine, but this compound could not be isolated with certainty.

In the case of 2′ : 6′-dibromo-4′-amino-3-phenyl-4-methylphthalaz-1-one, however, a similar reduction gave 2′-*bromo*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine* and 2 : 6-dibromo-*p*-phenylenediamine. All attempts to prepare 2′ : 6′-dibromo-4′-amino-*N*-phenyl-3-methylphthalimidine failed. Various reductions of 2′ : 6′-dibromo-4′-amino-3-phenyl-4-methylphthalaz-1-one with alkaline hydrosulphite indicated the existence of the intermediate 1-keto-3-(bromo-4′-aminophenyl)-4-methyltetrahydrophthalazine, but the only reaction product which could be isolated with certainty was 4′-amino-3-phenyl-4-methylphthalaz-1-one.

Finally, the 2′ : 6′-dihalogeno-4′-nitro-3-phenyl-4-methylphthalaz-1-ones react with methyl sulphate in a similar manner to the corresponding unhalogenated compound. The methylated bases are isolated as orange-red powders and crystallise from ethyl acetate or methyl alcohol in brownish-red prisms, m. p. 136° (dichloro-), and orange-red plates, m. p. 129° (dibromo-), in each case. These substances, probably 2′ : 6′-*dihalogeno*-4′-*nitro*-1-*methoxy*-3-*phenyl*-4-*methylene*-3 : 4-*dihydrophthalazines*, possess similar properties to those of the corresponding unhalogenated compound.

Further work on this subject is in progress.

EXPERIMENTAL.

The methods of preparing the analogous dichloro- and dibromo-compounds are in most cases so similar that separate descriptions are not necessary. In such cases the details in parentheses refer to the dibromo-compounds.

Sodium Hydrogen 3-(2′ : 6′-*Dichloro*- or -*dibromo*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate.*—A filtered solution of 50 g. of commercial 50% (60%) sodium β-naphthol-1-sulphonate in 120 c.c. (130 c.c.) of water was stirred at 0° into a solution of diazotised 2 : 6-dichloro-4-nitroaniline (2 : 6-dibromo-4-nitroaniline). The latter was obtained by adding 9·3 g. (11 g.) of sodium nitrite to a solution of 21 g. of 2 : 6-dichloro-4-nitroaniline (30 g. of 2 : 6-dibromo-4-nitroaniline) in 150 c.c. of cold concentrated sulphuric acid, followed by addition of ice with stirring, the temperature being kept below 10° (30°), until the volume was about 750 c.c. (800 c.c.). The diazo-solution was filtered from the unaltered base, 0·8—1·5 g. (2—3 g.). The 2′ : 6′-dihalogeno-4′-nitrobenzene-2-naphthol-1-diazosulphonate separated immediately as a chocolate-coloured precipitate, which was filtered more readily than when made at a higher temperature. It was washed free from acid with water, made into a paste with 200 c.c. of cold water, and stirred into a cold solution of 24 g. of anhydrous sodium carbonate in 60 c.c. of water. The orange solution produced [if it was kept, brownish-yellow needles or orange crystals of sodium 1-(2′ : 6′-dihalogeno-4′-nitrobenzeneazo)-β-naphthaquinone-1-sulphonate separated, after addition of salt in the case of the dibromo-compound] was added immediately to a cold solution of 20 g. of sodium hydroxide in 40 c.c. of water; the temperature rose about 10°, and the deep crimson (magenta-red) mixture was left overnight (2 days) until the colour had changed completely to yellowish-brown (brown). It was rendered faintly acid with hydrochloric acid, then made alkaline with sodium carbonate, the 2′ : 6′-dihalogeno-4′-nitrobenzeneazo-β-naphthol (3—5 g.) filtered off, and the filtrate rendered faintly acid with hydrochloric acid; the product separated almost completely as a yellow crystalline precipitate, a further quantity being obtained by adding salt to the filtrate. After drying, it was separated from sodium chloride by extraction with absolute alcohol and removal of the latter.

Sodium hydrogen 3-(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (yield, 37 g.; 75·6%, calculated on the 2 : 6-dichloro-4-nitroaniline) crystallised from water (charcoal) in small yellow needles or from ethyl acetate in small yellow prisms (Found : S, 6·9; Cl, 14·6. $C_{16}H_{10}O_7N_3Cl_2SNa$ requires S, 6·6; Cl, 14·7%). 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.

Sodium hydrogen 3-(2′ : 6′-*dibromo*-4′-*nitrophenyl*)-1 : 3-*dihydro*-

phthalazine-1-*sulphonate*-4-*acetate* crystallised from alcohol in orange prisms and from ethyl acetate in yellow leaflets (yield, 41·3 g.; 71·3%) (Found: Br, 28·0; S, 5·8. $C_{16}H_{10}O_7N_3Br_2SNa$ requires Br, 28·0; S, 5·6%). It was readily soluble in water, but less soluble in alcohol and ethyl acetate. The yellow aqueous solution deepened and reddened in colour on addition of alkalis, and was decolorised by zinc dust and ammonia, an orange colour returning on exposure to air.

1-*Hydroxy*-3-(2′ : 6′-*dichloro*- or -*dibromo*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—A solution of 20 g. of sodium hydrogen 3-(2′ : 6′-dichloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-1-sulphonate-4-acetate (35 g. of the corresponding dibromo-compound) in 60 c.c. (200 c.c.) of water was boiled with 32 c.c. (200 c.c.) of concentrated hydrochloric acid until evolution of sulphur dioxide had ceased, and the product, which separated first as an oil, had formed yellowish-brown crystals. The latter were washed with boiling water and recrystallised from ethyl acetate. 1-*Hydroxy*-3-(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* formed orange-yellow irregular prisms, m. p. 245° (yield, 14·5 g.; 88%) (Found: C, 48·3; H, 2·8; N, 10·7; Cl, 17·7. $C_{16}H_{11}O_5N_3Cl_2$ requires C, 48·5; H, 2·8; N, 10·6; Cl, 17·9%), readily soluble in alcohol, acetone, or glacial acetic acid, but almost insoluble in benzene or ether.

1-*Hydroxy*-3-(2′ : 6′-*dibromo*-4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* formed yellow hexagonal prisms, m. p. 245° (yield, 24 g.; 80·7%) (Found: C, 39·4; H, 2·5; N, 8·6; Br, 33·1. $C_{16}H_{11}O_5N_3Br_2$ requires C, 39·6; H, 2·3; N, 8·7; Br, 33·0%), readily soluble in alcohol, but less soluble in benzene and glacial acetic acid.

Both acids are sparingly soluble in water, forming solutions acid to litmus, but dissolve readily in sodium carbonate or hydroxide with a deep red or brownish-red colour, and prolonged boiling of the alkaline solutions causes decomposition. They dissolve in cold concentrated sulphuric acid with an orange-yellow or yellow colour and are reprecipitated unaltered on dilution, but when boiled with aqueous sulphuric acid they are converted into the 2′ : 6′-dihalogeno-4′-nitro-3-phenylphthalaz-1-ones.

The esters. A solution of 5 g. (3 g.) of the acid in 50 c.c. of dry methyl alcohol was saturated with dry hydrogen chloride at 0°, left over-night, and then boiled under reflux for 2 hours. The *methyl* ester of the dichloro-compound crystallised from methyl alcohol in brownish-yellow needles containing methyl alcohol of crystallisation, or from benzene in yellow, vitreous, rhombic prisms, softening at 110—140° and melting at 167—168°, containing 1 mol. benzene of crystallisation, or m. p. 169° after removal of the benzene

(Found : loss at 110°, 16·0. $C_{17}H_{13}O_5N_3Cl_2,C_6H_6$ requires C_6H_6, 15·9%. Found in material dried at 110° : C, 50·0; H, 3·3; N, 10·4. $C_{17}H_{13}O_5N_3Cl_2$ requires C, 49·8; H, 3·2; N, 10·2%). The *ethyl* ester, similarly prepared, crystallised from benzene in yellow, vitreous, rhombic prisms, softening at 80—100° and melting at 160—161°, containing 1 mol. benzene of crystallisation, partially lost at air temperature and removed completely at 100° (m. p. 162°) (Found : loss at 100°, 14·3. $C_{18}H_{15}O_5N_3Cl_2,C_6H_6$ requires C_6H_6, 15·5%. Found in material dried at 100° : C, 51·3; H, 3·6; N, 10·1; Cl, 17·1. $C_{18}H_{15}O_5N_3Cl_2$ requires C, 50·9; H, 3·5; N, 9·9; Cl, 16·8%). The *methyl* ester of the dibromo-compound crystallised from methyl alcohol in orange-yellow needles, m. p. 176° (Found : C, 41·2; H, 2·9. $C_{17}H_{13}O_5N_3Br_2$ requires C, 40·9; H, 2·6%). The *ethyl* ester, similarly prepared, crystallised from ethyl alcohol in long yellow prisms containing 1 mol. alcohol of crystallisation, partially lost at air temperature and removed completely at 115°; it then melted at 182° (Found : loss at 115°, 7·2. $C_{18}H_{15}O_5N_3Br_2,C_2H_6O$ requires C_2H_6O, 8·2%. Found in material dried at 115° : C, 42·3; H, 3·2. $C_{18}H_{15}O_5N_3Br_2$ requires C, 42·1; H, 2·9%). The four esters are insoluble in sodium carbonate, but dissolve in sodium hydroxide solution with a reddish-brown colour.

Acetyl derivative of the dichloro-acid. A solution of 5 g. of the acid in 10 c.c. of glacial acetic acid was boiled with 5 c.c. of acetic anhydride under reflux for 8 hours and then poured on ice. The resinous product, after repeated crystallisations from ethyl alcohol (charcoal), formed yellow, vitreous, irregular prisms, melting at 110—112°, resolidifying and melting at 202—204°, containing 1 mol. ethyl alcohol of crystallisation, which was difficult to remove without partial decomposition (Found : loss at 100°, 9·8. $C_{18}H_{13}O_6N_3Cl_2,C_2H_6O$ requires C_2H_6O, 9·5%. Found in material dried at 100° : N, 9·8; Cl, 16·1. $C_{18}H_{13}O_6N_3Cl_2$ requires N, 9·6; Cl, 16·2%). It dissolved in sodium carbonate solution with an orange-brown colour and in sodium hydroxide with a brownish-red colour.

Anilides. A fine suspension of 4 g. of the dichloro-acid in 400 c.c. of toluene was boiled with 2 g. of aniline and 1 g. of phosphorus trichloride under reflux for 5 hours with stirring. When cold, the residue was washed with a little sodium carbonate solution and crystallised from glacial acetic acid, forming clusters of small yellow needles, m. p. 289° (Found : C, 56·0; H, 3·4; N, 12·1; Cl, 15·1. $C_{22}H_{16}O_4N_4Cl_2$ requires C, 56·0; H, 3·4; N, 11·9; Cl, 15·1%). The *anilide* of the dibromo-acid, similarly prepared, formed yellow plates, m. p. 280°, after several crystallisations from glacial acetic acid (Found : C, 47·0; H, 3·1; N, 10·2. $C_{22}H_{16}O_4N_4Br_2$ requires C, 47·1; H, 2·9; N, 10·0%). Both anilides are insoluble in cold sodium hydroxide solution.

1-*Hydroxy*-3-(2′ : 6′-*dichloro*- or -*dibromo*-4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic Acid*.—A mixture of 25 g. (20 g.) of the finely powdered nitro-compound with a solution of 80 g. of stannous chloride in 200 c.c. of concentrated hydrochloric acid was boiled until the yellow compound dissolved and the hydrochloride of the 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-aminophenyl) - tetrahydrophthalazine-4-acetic acid began to crystallise in colourless plates (needles). After cooling, the hydrochloride was filtered off, washed with cold concentrated hydrochloric acid, and dissolved in dilute sodium carbonate solution. The solution was filtered, and the product isolated by addition of dilute hydrochloric acid until a white precipitate had separated completely. 1-*Hydroxy*-3-(2′ : 6′-*dichloro*-4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic acid* crystallised from ethyl acetate in almost colourless, rhombic prisms, m. p. 242° (decomp.) (yield, 18·1 g.; 78%) (Found: C, 52·5; H, 3·9; N, 11·4; Cl, 19·4. $C_{16}H_{15}O_3N_3Cl_2$ requires C, 52·2; H, 4·1; N, 11·6; Cl, 19·3%), insoluble in benzene and very sparingly soluble in water; it gave no coloration with ferric chloride.

1-*Hydroxy*-3-(2′ : 6′-*dibromo*-4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic acid* crystallised from ethyl acetate in colourless cubes, m. p. 261° (yield, 15 g.; 79·5%) (Found: C, 42·2; H, 3·2; N, 9·3. $C_{16}H_{15}O_3N_3Br_2$ requires C, 42·0; H, 3·3; N, 9·2%), very sparingly soluble in water; although it was more soluble in alcohol and glacial acetic acid than in ethyl acetate, these solvents lower the melting point, probably owing to partial esterification and acetylation respectively. Both acids dissolve readily in dilute alkali solutions. The dichloro-acid is less readily soluble in dilute acids than the dibromo-acid; the mineral acid salts crystallise slowly from the former, and immediately from the latter, solutions, and can be diazotised. Heating with aqueous alkalis converts both acids into the 2′ : 6′-dihalogeno-4′-amino-3-phenyl- 4 - methylphthalaz - 1 - ones. The *acetyl* derivative of the dichloro-compound crystallised from alcohol in colourless prisms, m. p. 282° (decomp.) (Found: C, 52·7; H, 3·9; Cl, 17·4. $C_{18}H_{17}O_4N_3Cl_2$ requires C, 52·7; H, 4·1; Cl, 17·3%). The *acetyl* derivative of the dibromo-compound crystallised from glacial acetic acid in almost colourless plates, m. p. 270° (Found: C, 43·4; H, 3·3; Br, 32·0. $C_{18}H_{17}O_4N_3Br_2$ requires C, 43·3; H, 3·4; Br, 32·1%).

2′ : 6′-*Dichloro*- or -*dibromo*-4′-*amino*-3-*phenylphthalaz*-1-*one*.—A solution of 10 g. of 1-hydroxy-3-(2′ : 6′-dichloro-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (5 g. of the dibromo-compound) in 50 c.c. (25 c.c.) of concentrated sulphuric acid and 60 c.c. (30 c.c.)

of water was boiled under reflux for 2 hours (1 hour), acetic acid being eliminated. The solution was diluted with 100 c.c. (60 c.c.) of water, boiled (charcoal), and filtered. On cooling, the sulphate of 2′ : 6′-dichloro-4′-amino-3-phenylphthalaz-1-one crystallised in pale yellow prisms; it was converted into the base with sodium carbonate, and a further quantity of less pure base was precipitated by neutralising the acid filtrate. (The sulphate of the dibromo-compound did not crystallise, and the base was obtained by neutralising the cold filtrate with sodium hydroxide.)

2′ : 6′-*Dichloro*-4′-*amino*-3-*phenylphthalaz*-1-*one* crystallised from alcohol (charcoal) in yellow rhombic prisms, m. p. 302° (yield, 6·4 g.; 77%) (Found : C, 54·9; H, 3·1; Cl, 23·1. $C_{14}H_9ON_3Cl_2$ requires C, 54·9; H, 2·9; Cl, 23·2%). The hydrochloride formed colourless plates, and the *acetyl* derivative crystallised from alcohol in colourless prismatic needles, m. p. 334°, which became bluish-green on the surface on exposure to light (Found : C, 55·3; H, 3·3; Cl, 20·5. $C_{16}H_{11}O_2N_3Cl_2$ requires C, 55·2; H, 3·2; Cl, 20·4%).

2′ : 6′-*Dibromo*-4′-*amino*-3-*phenylphthalaz*-1-*one* crystallised from alcohol in deep yellow plates, m. p. 304° (yield, 3·5 g.; 81%) (Found : C, 42·7; H, 2·2. $C_{14}H_9ON_3Br_2$ requires C, 42·5; H, 2·3%), and from glacial acetic acid in almost colourless needles containing 1 mol. acetic acid, m. p. 315° (Found : Br, 35·4. $C_{14}H_9ON_3Br_2,C_2H_4O_2$ requires Br, 35·2%). The *acetyl* derivative crystallised from glacial acetic acid in clusters of small brownish prismatic needles, m. p. 338° (Found : C, 43·8; H, 2·8. $C_{16}H_{11}O_2N_3Br_2$ requires C, 43·9; H, 2·5%). The powdered substance became blue on exposure to light.

2′ : 6′-*Dichloro*-4′-*amino*-N-*phenylphthalimidine*.—A solution of 4 g. of 2′ : 6′-dichloro-4′-amino-3-phenylphthalaz-1-one in 100 c.c. of water and 160 c.c. of concentrated hydrochloric acid was boiled vigorously while 6 g. of zinc dust were added in small portions during ½ hour. (Boiling for a longer time results in decomposition and 2 : 6-dichloro-*p*-phenylenediamine can be detected.) After cooling, the solution was almost neutralised with sodium hydroxide, and the yellowish precipitate filtered off; the filtrate contained ammonia. The *base* crystallised from alcohol (charcoal) in almost colourless, flat prisms, m. p. 253° (yield, 2·4 g.; 62·6%) (Found : C, 57·5; H, 3·6; Cl, 24·4. $C_{14}H_{10}ON_2Cl_2$ requires C, 57·3; H, 3·4; Cl, 24·2%). The hydrochloride formed colourless prisms, and the *acetyl* derivative crystallised from alcohol in colourless rhombic prisms, m. p. 239° (Found : C, 57·5; H, 3·8; Cl, 21·0. $C_{16}H_{12}O_2N_2Cl_2$ requires C, 57·3; H, 3·6; Cl, 21·2%).

2′ : 6′-*Dichloro*-N-*phenylphthalimidine*.—A solution of 4 g. of the amino-derivative in 28 c.c. of concentrated sulphuric acid at 0°

was diazotised by addition of 1 g. of sodium nitrite, followed by ice until the volume was about 110 c.c. The diazo-sulphate (almost colourless crystals) was boiled with 400 c.c. of alcohol; the 2′ : 6′-*dichloro*-N-*phenylphthalimidine* obtained crystallised in brownish rhombic prisms, m. p. 146° (Found : C, 60·3; H, 3·3; Cl, 25·4. $C_{14}H_9ONCl_2$ requires C, 60·4; H, 3·2; Cl, 25·5%).

Reduction of 2′ : 6′-*Dibromo*-4′-*amino*-3-*phenylphthalaz*-1-*one.*—(a) 4′-*Amino*-N-*phenylphthalimidine.* A solution of 4 g. of 2′ : 6′-dibromo-4′-amino-3-phenylphthalaz-1-one in 600 c.c. of water and 100 c.c. of concentrated hydrochloric acid was boiled and zinc dust added in small portions until a colourless solution was obtained. On concentration to about 50 c.c., the zinc double chloride crystallised in colourless needles. It was converted into 4′-amino-*N*-phenylphthalimidine, almost colourless, prismatic needles, m. p. 198° (total yield, 0·6 g.; 26·5%) as previously described (J., 1926, 704), the identity being confirmed by its conversion into the acetyl derivative, fine colourless needles, m. p. 272° (not 196° as previously given erroneously; *loc. cit.*) (Found : C, 72·3; H, 5·6. Calc. for $C_{16}H_{14}O_2N_2$: C, 72·2; H, 5·3%). The filtrate from the zinc double chloride of 4′-amino-*N*-phenylphthalimidine was neutralised and filtered, the dry precipitate extracted with alcohol, and the alcohol distilled. The residue was a mixture of 4′-amino-*N*-phenylphthalimidine and a little of its 2′-bromo-derivative (see below), from which the latter was separated by means of the greater solubility of its hydrochloride in hydrochloric acid.

(b) 2′-*Bromo*-4′-*amino*-N-*phenylphthalimidine.* A fine suspension of the hydrochloride, obtained by grinding 4 g. of 2′ : 6′-dibromo-4′-amino-3-phenylphthalaz-1-one with 100 c.c. of concentrated hydrochloric acid, was boiled gently and 5 g. of zinc dust were added in small portions during ½ hour with vigorous stirring. After 12 hours, the liquid was filtered from the hydrochlorides of unaltered 2′ : 6′-dibromo-4′-amino-3-phenylphthalaz-1-one and any 4′-amino-*N*-phenylphthalimidine, diluted, and rendered alkaline with sodium carbonate, and the dry precipitate extracted with alcohol (charcoal). Fractional crystallisation gave the *base* in colourless rhombic crystals, containing alcohol of crystallisation, rapidly lost at air temperature, m. p. 178° after removal of the solvent (Found : C, 55·2; H, 3·8; Br, 26·2. $C_{14}H_{11}ON_2Br$ requires C, 55·4; H, 3·6; Br, 26·4%). The *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 272° (Found : C, 55·5; H, 3·8. $C_{16}H_{13}O_2N_2Br$ requires C, 55·7; H, 3·8%).

2′ : 6′-*Dichloro*- or -*dibromo*-4′-*nitro*-3-*phenylphthalaz*-1-*one* (I).—A solution of 10 g. of 1-hydroxy-3-(2′ : 6′-dichloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (10 g. of the dibromo-compound) in 40 c.c. (50 c.c.) of concentrated sulphuric acid was diluted with 48 c.c. (60 c.c.) of water and boiled under reflux for 2 hours ($1\frac{1}{2}$ hours). The yellow precipitate slowly dissolved and acetic acid was eliminated. The brown solution was cooled, diluted with 100 c.c. (120 c.c.) of water, boiled (charcoal), and filtered. After cooling, the sulphate which separated in colourless prisms (cream-coloured plates, m. p. 283°), was filtered off and neutralised with sodium carbonate. A further quantity, but less pure, was isolated by almost neutralising the filtrate. 2′ : 6′-*Dichloro*-4′-*nitro*-3-*phenylphthalaz*-1-*one* crystallised from glacial acetic acid in pale yellow needles, m. p. 315° (decomp.) (yield, 5·4 g.; 63·6%) (Found: C, 49·8; H, 2·0; N, 12·5; Cl, 21·2. $C_{14}H_7O_3N_3Cl_2$ requires C, 50·0; H, 2·1; N, 12·5; Cl, 21·1%), readily soluble in glacial acetic acid and pyridine, sparingly soluble in alcohol, and almost insoluble in benzene.

2′ : 6′-*Dibromo*-4′-*nitro*-3-*phenylphthalaz*-1-*one* crystallised from alcohol in almost colourless needles, m. p. 306° (yield, 7·5 g.; 85·5%), and from glacial acetic acid in cream-coloured plates, containing 1 mol. acetic acid, m. p. 306° (Found: loss at 130°, 12·3. $C_{14}H_7O_3N_3Br_2,C_2H_4O_2$ requires $C_2H_4O_2$, 12·4%. Found in material dried at 130°: C, 39·4; H, 1·8; N, 10·0. $C_{14}H_7O_3N_3Br_2$ requires C, 39·5; H, 1·6; N, 9·9%).

Both bases are insoluble in sodium carbonate solution, and both give with an alcoholic solution of picric acid *picrates*, yellow plates, m. p. 233° (Found: N, 15·0. $C_{20}H_{10}O_{10}N_6Cl_2$ requires N, 14·9%), and deep yellow needles, m. p. 252° (Found: N, 13·1. $C_{20}H_{10}O_{10}N_6Br_2$ requires N, 12·8%).

Reduction. (*a*) A fine suspension of 4 g. of 2′ : 6′-dichloro-4′-nitro-3-phenylphthalaz-1-one (2 g. of the dibromo-compound) in 100 c.c. (50 c.c.) of water was heated to 75° with a solution of 30 g. (8 g.) of sodium sulphide crystals in 30 c.c. (8 c.c.) of water, and the bluish-red mixture was then boiled for 10 minutes until the colour had changed to yellowish-brown. The 2′ : 6′-dihalogeno-4′-amino-3-phenylphthalaz-1-one (yield of the dichloro-compound, 1·5 g.; 41·2%) separated, identical with that obtained from the 1-hydroxy-3-(2′ : 6′-dihalogeno-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (p. 1082).

(*b*) Reduction with zinc dust and hydrochloric acid converted the dichloro-compound into 2′ : 6′-dichloro-4′-amino-*N*-phenylphthalimidine (yield, 55%), identical with that obtained from 2′ : 6′-dichloro-4′-amino-3-phenylphthalaz-1-one (p. 1082), and the dibromo-compound into 4′-amino-*N*-phenylphthalimidine, identical with that obtained from 2′ : 6′-dibromo-4′-amino-3-phenylphthalaz-1-one (p. 1083).

Action of methyl sulphate. A solution of 12 g. of 2′ : 6′-dichloro-4′-nitro-3-phenylphthalaz-1-one (14 g. of the dibromo-compound) in 150 c.c. of dry nitrobenzene was heated under reflux at 130° for 1 hour, 5 g. (4·2 g.) of methyl sulphate being added during the first ¼ hour. Nitrobenzene was removed by distillation with steam, and the aqueous residue, after cooling, gave an orange-yellow precipitate (probably II), 11 g. (15 g., m. p. 217°), when rendered alkaline with sodium carbonate. The basic substance obtained from the dichloro-compound crystallised from ethyl acetate in orange plates, m. p. 235° (Found : C, 50·9; H, 3·1; OMe, 8·4%), from methyl alcohol in orange prisms, m. p. 157° (Found : C, 49·1; H, 3·6; OMe, 14·7%), and from ethyl alcohol in orange prisms, m. p. 111° (see p. 1075). The basic substance obtained from the dibromo-compound crystallised from ethyl acetate in orange-yellow plates, m. p. 228° (decomp.) (Found : C, 40·6, 40·7; H, 2·5, 2·4; OMe, 6·7%), from methyl alcohol in orange prisms, m. p. 138° [Found : C, 40·75, 40·95; H, 3·0, 3·1; OMe, 12·9 (freshly prepared material), 11·8 (material 1 week old). $C_{16}H_{13}O_4N_3Br_2$ requires C, 40·8; H, 2·8; OMe, 13·2%], and from ethyl alcohol in orange prisms, m. p. 110—112°.

2′ : 6′-*Dichloro-* or *-dibromo-*4′*-nitro-*3*-phenyl-*4*-methylphthalaz-*1*-one.*—A solution of 6 g. of 1-hydroxy-3-(2′ : 6′-dichloro-4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (5 g. of the dibromo-compound) in 60 c.c. of cold concentrated sulphuric acid was poured on 125 g. (130 g.) of ice, and 3 g. (2 g.) of powdered sodium (potassium) dichromate were added as described for the corresponding unhalogenated compound (this vol., p. 1070). Next day, the solution was filtered, and almost neutralised (with cooling), and the pale yellowish precipitate produced was washed with water, and dried. 2′ : 6′-*Dichloro-*4′*-nitro-*3*-phenyl-*4*-methylphthalaz-*1*-one* crystallised from alcohol or dilute acetic acid in greenish-yellow prisms or needles, m. p. 240° (decomp.) (yield, 4 g.; 75·5%) (Found : C, 51·6; H, 2·7; N, 12·3; Cl, 20·1. $C_{15}H_9O_3N_3Cl_2$ requires C, 51·4; H, 2·6; N, 12·0; Cl, 20·3%).

2′ : 6′-*Dibromo-*4′*-nitro-*3*-phenyl-*4*-methylphthalaz-*1*-one* crystallised from alcohol in greenish-yellow prisms, m. p. 254° (yield, 1·3 g.; 28·7%) (Found : C, 41·0; H, 2·3; N, 9·8; Br, 36·6. $C_{15}H_9O_3N_3Br_2$ requires C, 41·0; H, 2·1; N, 9·6; Br, 36·4%). Both substances are insoluble in sodium carbonate solution, and both give with an alcoholic solution of picric acid *picrates*, yellow needles, m. p. 225° (Found : N, 14·8. $C_{21}H_{12}O_{10}N_6Cl_2$ requires N, 14·5%), and yellow prisms, m. p. 215° (Found : C, 37·5; H, 2·0. $C_{21}H_{12}O_{10}N_6Br_2$ requires C, 37·7; H, 1·8%).

Action of methyl sulphate. A solution of 3·5 g. of 2′ : 6′-dichloro-

4′-nitro-3-phenyl-4-methylphthalaz-1-one (4·5 g. of the dibromo-compound) in 50 c.c. of hot dry nitrobenzene was treated with 1·5 g. (1·4 g.) of methyl sulphate as described for the corresponding unhalogenated compound (*ibid.*, p. 1071). The orange-red basic products were probably 2′ : *6′-dichloro-4′-nitro-*1*-methoxy-*3*-phenyl-*4*-methylene-*3 : 4*-dihydrophthalazine*, which crystallised from ethyl acetate or methyl alcohol in brownish-red rectangular prisms, m. p. 136° (Found: C, 52·7; H, 3·1; N, 11·2; Cl, 19·1; OMe, 9·1. $C_{16}H_{11}O_3N_3Cl_2$ requires C, 52·7; H, 3·0; N, 11·5; Cl, 19·5; OMe, 8·5%), and 2′ : *6′-dibromo-4′-nitro-*1*-methoxy-*3*-phenyl-*4*-methylene-*3 : 4*-dihydrophthalazine*, which crystallised from ethyl acetate or methyl or ethyl alcohol in orange-red plates, m. p. 129° (Found: C, 42·5; H, 2·7; N, 8·9; Br, 34·9; OMe, 7·2. $C_{16}H_{11}O_3N_3Br_2$ requires C, 42·4; H, 2·4; N, 9·2; Br, 35·3; OMe, 6·8%). Both substances are insoluble in sodium hydroxide solution, but dissolve readily in mineral acids.

2′ : *6′-Dichloro- or -dibromo-4′-amino-*3*-phenyl-*4*-methylphthalaz-*1*-one.*—(*a*) A solution of 1-hydroxy-3-(2′:6′-dichloro-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (10 g.) in cold concentrated sulphuric acid (20 c.c.) was poured into water (100 c.c.), and the mixture treated with powdered sodium dichromate (3·5 g.) as described for the corresponding unhalogenated compound (*loc. cit.*). The greenish-yellow mixture was submitted to filtration, the filtrate neutralised with sodium hydroxide, and the precipitate filtered off. In the case of the dibromo-compound a solution of 5 g. of 1-hydroxy-3-(2′ : 6′-dibromo-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid in 20 c.c. of cold concentrated sulphuric acid was poured on 100 g. of ice, and the white suspension was stirred mechanically for 2 hours while a solution of 1·2 g. of sodium dichromate in 20 c.c. of water was added drop by drop; after 4 hours, the yellowish-green solution was almost neutralised with sodium hydroxide, and the precipitate filtered off. The product in both cases was dissolved in boiling dilute hydrochloric acid (charcoal); pale yellow needles separated when the warm filtered solution was rendered alkaline with sodium hydroxide. 2′ : *6′-Dichloro-4′-amino-*3*-phenyl-*4*-methylphthalaz-*1*-one* crystallised from alcohol in pale yellow plates, m. p. 325° (yield, 6·3 g.; 72·5%) (Found: C, 56·2; H, 3·6; N, 13·3; Cl, 22·4. $C_{15}H_{11}ON_3Cl_2$ requires C, 56·2; H, 3·4; N, 13·1; Cl, 22·2%), readily soluble in pyridine, but sparingly soluble in ethyl acetate.

2′ : *6′-Dibromo-4′-amino-*3*-phenyl-*4*-methylphthalaz-*1*-one* crystallised from alcohol in pale yellow needles, m. p. 315° (yield, 3·2 g.; 74%) (Found: C, 43·9; H, 2·9; N, 10·4; Br, 39·0. $C_{15}H_{11}ON_3Br_2$ requires C, 44·0; H, 2·7; N, 10·3; Br, 39·1%).

(*b*) A solution of 3 g. of 1-hydroxy-3-(2′ : 6′-dichloro-4′-

aminophenyl)-tetrahydrophthalazine-4-acetic acid (4 g. of the dibromo-compound) in 30 c.c. of water and 3 g. of sodium hydroxide (150 c.c of 10% sodium carbonate solution: a solution of sodium hydroxide also can be used, but the product is less pure) was heated under reflux at about 90° for 8 hours (boiled under reflux for 2½ hours); the product separated progressively in needles (brownish plates), the yield being 1·8 g., *i.e.*, 69%, after recrystallisation from alcohol (1·3 g.; 36·3%).

(*c*) Reduction of the 2′ : 6′-dihalogeno-4′-nitro-3-phenyl-4-methylphthalaz-1-ones with aqueous sodium sulphide as described for the corresponding unhalogenated compound (*loc. cit.*) also gave the 2′ : 6′-dihalogeno-4′-amino-3-phenyl-4-methylphthalaz-1-ones. The reduction of the dibromo-compound was difficult to control (yield, 28%), much of the nitro-compound remaining unaltered.

(*d*) A solution of 5·4 g. of 1-hydroxy-3-(2′ : 6′-dibromo-4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid in 100 c.c. of water and 100 c.c. of saturated sodium carbonate solution was boiled, and 125 c.c. of 2·5% potassium permanganate solution were added slowly beneath the surface. The product separated immediately in straw-coloured needles (yield, 4 g.; 82·7%).

The *acetyl* derivative of the dichloro-compound crystallised from alcohol in clusters of colourless flat prisms, m. p. 311°, which became blue on the surface on exposure to light (Found: C, 56·6; H, 3·8; N, 11·7; Cl, 19·6. $C_{17}H_{13}O_2N_3Cl_2$ requires C, 56·4; H, 3·6; N, 11·6; Cl, 19·6%). The *acetyl* derivative of the dibromo-compound crystallised from alcohol in colourless plates, m. p. 315°, which became blue on the surface on exposure to light (Found: C, 45·1; H, 3·2; N, 9·4; Br, 35·2. $C_{17}H_{13}O_2N_3Br_2$ requires C, 45·2; H, 2·9; N, 9·3; Br, 35·5%).

Reduction of 2′ : 6′-*Dichloro*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one.*—(*a*) Reduction of this compound (4 g.) with zinc dust and hydrochloric acid as described for the preparation of 2′ : 6′-dichloro-4′-amino-*N*-phenylphthalimidine (p. 1083) gave a resinous product, from which only 2 : 6-dichloro-*p*-phenylenediamine, almost colourless needles, m. p. 123° (yield, 1 g.; 45·2%), could be isolated. (*b*) Treatment of a suspension of 2′ : 6′-dichloro-4′-amino-3-phenyl-4-methylphthalaz-1-one in boiling aqueous or aqueous-alcoholic sodium hydroxide with sodium hydrosulphite under various conditions gave mixtures, from which only the unaltered substance could be isolated with certainty, although traces of a substance, faintly coloured, hexagonal prisms, m. p. 227°, possibly 1-keto-3-(2′ : 6′-dichloro-4′-aminophenyl)-4-methyltetrahydrophthalazine, were obtained, but not sufficient for analysis.

Reduction of 2′ : 6′-*Dibromo*-4′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one*.—(*a*) 2′-*Bromo*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine*. A solution of 8 g. of the dibromo-compound in 200 c.c. of water and 200 c.c. of concentrated hydrochloric acid was boiled, and 20 g. of zinc dust were added in small portions. The solution was concentrated, and rendered alkaline with sodium carbonate, and the dry precipitate extracted with alcohol. The alcoholic solution (charcoal) was filtered, and the filtrate precipitated with water. Fractional crystallisation of the dry precipitate from toluene gave some 2′-*bromo*-4′-*amino*-N-*phenyl*-3-*methylphthalimidine* in colourless prismatic needles, m. p. 216° (Found : C, 56·6; H, 4·4; N, 8·6; Br, 25·0. $C_{15}H_{13}ON_2Br$ requires C, 56·8; H, 4·1; N, 8·8; Br, 25·2%). The *acetyl* derivative crystallised from alcohol in colourless prisms, m. p. 266° (Found : C, 57·0; H, 4·4. $C_{17}H_{15}O_2N_2Br$ requires C, 56·8; H, 4·2%). 2 : 6-Dibromo-*p*-phenylenediamine, almost colourless needles, m. p. 139°, also was isolated, and particularly readily from other reduction mixtures in which the proportions of acid and zinc were decreased in the attempt to control the reaction. (*b*) Treatment of a suspension of 2′ : 6′-dibromo-4′-amino-3-phenyl-4-methylphthalaz-1-one in boiling aqueous-alcoholic sodium hydroxide with sodium hydrosulphite under various conditions gave mixtures from which only the unaltered substance and 4′-amino-3-phenyl-4-methylphthalaz-1-one, m. p. 277°, could be isolated with certainty, although traces of two substances containing bromine (yellow prisms, m. p. 228°; yellow plates, m. p. 218°) were obtained, but not sufficient for analysis (compare this vol., p. 1072).

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