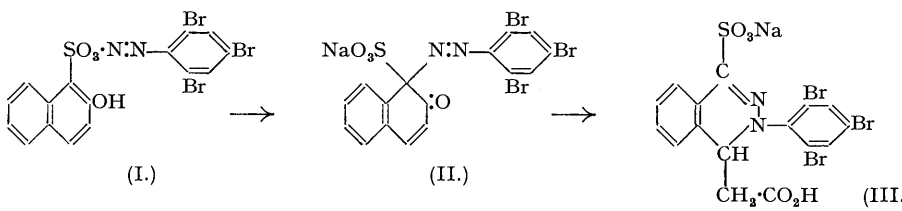
123. *A Reaction of Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part XXIV. The Phthalazine Reaction with Bases not containing a Nitro-group. Derivatives of Halogenobenzene-2-naphthol-1-diazosulphonates.**

By A. T. Peters, G. T. Pringle, and (the late) F. M. Rowe.

In Part I of this Series (*J.*, 1926, 692), it was stated that the only diazosulphonates not containing a nitro-group which are convertible into phthalazine derivatives are those derived from 4-aminoazobenzene. It is now shown that the reaction is more general, and phthalazine compounds are obtainable from 2′ : 4′ : 6′-tribromo- and 3′- and 4′-chloro-benzene-2-naphthol-1-diazosulphonate. The derived 1-*hydroxy*-3-*halogenophenyl*-3 : 4-*dihydrophthalazine*-4-*acetic acids* show similar reactions to those of other analogues in this series, but several anomalies are noted.

Conversion of 2′ : 4′ : 6′-tribromobenzene-2-naphthol-1-diazosulphonate (I) into the 1-(2′ : 4′ : 6′-tribromobenzeneazo)-β-naphthaquinone-1-sulphonate (II) is slow, but is accelerated by alcohol at 40°, as also is the subsequent action of sodium hydroxide on the latter to form *sodium hydrogen* 3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (III). No trace of

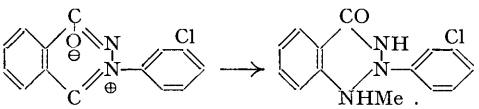


sodium benzaldehyde 2′ : 4′ : 6′-tribromophenylhydrazone-ω-sulphonate-2-β-acrylic acid was detected. Acid hydrolysis of the above sodium salt furnished 1-*hydroxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid* (IV), and the 3′- and 4′-*chlorophenyl* analogues were prepared similarly. All were converted by aqueous sulphuric acid (b. p. 140°) into the corresponding *halogeno*-3-*phenylphthalaz*-1-*ones*, or by cold acid dichromate into the respective *halogeno*-3-*phenyl*-4-*methylphthalaz*-1-*ones*. 1-*Methoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine* and chloro-2 : 4-dinitrobenzene or 1-phenyl-3-methyl-4-anilinomethylene-5-pyrazolone afforded 1-*methoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-4-(2″ : 4″-*dinitrobenzylidene*)- or -4-(5″-*keto*-1″-*phenyl*-3″-*methylpyrazolinylidene-ethylidene*)-3 : 4-*dihydrophthalazine*, respectively.

In general, the reactions of (IV) and its analogues follow the expected courses, and are recorded in the experimental section. Several anomalies, however, occur. Thus, Clemmensen reduction of 3′- and 4′-*chloro*-3-*phenylphthalaz*-1-*one* afforded 3′- and 4′-*chloro*-N-*phenylphthalimidine* respectively, but, in a similar reaction, 2′ : 4′ : 6′-*tribromo*-3-*phenylphthalaz*-1-*one* lost a bromine atom to yield 2′ : 4′-*dibromo*-N-*phenylphthalimidine*. Fission occurred during the Clemmensen

* The nomenclature in this paper follows that of earlier papers of the series.

reduction of 2′ : 4′ : 6-*tribromo*-3-*phenyl*-4-*methylphthalaz*-1-*one*, with formation of 2 : 4: 6-tribromoaniline; 3′-*chloro*-3-*phenyl*-4-*methylphthalaz*-1-*one* (V), however, yielded 1-*keto*-3-(3′-*chlorophenyl*)-4-*methyltetrahydrophthalazine* (VI), whilst a similar reduction of the 4′-*chloro*-analogue (VII) of (V) gave 4′-*chloro*-N-*phenyl*-3-*methylphthalimidine* (VIII).



With aqueous potassium permanganate at 70°, (IV) afforded 1 : 4-*diketo*-3-(2′ : 4′ : 6′-*tribromophenyl*)*tetrahydrophthalazine* (IX); the retention of all the bromine in this vigorous reaction is noteworthy, in view of the fact that bromine is lost during a similar reaction with the 2 : 6-dibromo-4-nitro-analogue (cf. *J.*, 1935, 1808).

Compound (IX) could not be methylated through its silver salt, but 1-*methoxy*-4-*keto*-3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine* was conveniently prepared by refluxing 1-methoxy-3-(2′ : 4′ : 6′-tribromophenyl)-4-methylene-3 : 4-dihydrophthalazine with *p*-nitrosodimethylaniline in alcohol.

Rowe, Adams, and Peters (*J.*, 1937, 9) noted the retarding influence of halogen on the conversion of nitroaryl-3-phenylphalaz-1-ones and their 1-methyl homologues into the isomeric 4-ones. When 2′ : 4′ : 6′-tribromo- and 3′-chloro-3-phenylphthalaz-1-one and their 4-methyl-derivatives were heated with aqueous hydrochloric acid (1 : 8) in a sealed tube at 190—200° for 6 hours, only unchanged material was recovered; prolonged reaction, *e.g.*, for 60 hours, caused considerable isomerisation with the 3′-chloro-derivatives, but only slight with the 2′ : 4′ : 6′-tribromo-compounds. The derived products were shown to be identical with synthetic specimens of 2′ : 4′ : 6′-*tribromo*- and 3′-*chloro*-3-*phenylphthalaz*-4-*one* and their 1-*methyl* derivatives respectively.

Experimental.

Sodium Hydrogen 3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (III).—A filtered solution of commercial 50% sodium β-naphthol-1-sulphonate (50 g.) in water (250 c.c.) was stirred at 0° into a solution of diazotised 2 : 4 : 6-tribromoaniline, prepared by dissolving dry sodium nitrite (9 g.) in concentrated sulphuric acid (150 c.c.) at 50° and adding the base (33 g.) to it, followed by pouring the mixture on ice (400 g.), with stirring. The straw-coloured precipitate of 2′ : 4′ : 6′-tribromobenzene-2-naphthol-1-diazosulphonate was washed free from acid with brine, mixed with cold water (200 c.c.), and powdered sodium carbonate added. After addition of 30 g., the resulting suspension of sodium 1-(2′ : 4′ : 6′-tribromobenzeneazo)-β-naphthaquinone-1-sulphonate was added to a solution of sodium hydroxide (60 g.) in ice-cold water, and the mixture left overnight. It was then acidified with concentrated hydrochloric acid and made alkaline with sodium carbonate solution. After removal of the 2′ : 4′ : 6′-tribromobenzeneazo-β-naphthol (4·5 g.; 8·6%) by filtration, it was acidified again and the *sodium hydrogen* salt was collected; it crystallised from water in minute colourless prisms (50 g.; 82%). It lost water of crystallisation at 120° (Found : loss at 120°, 10·4. $C_{16}H_{10}O_5N_2Br_3SNa,4H_2O$ requires H_2O, 10·6%. Found in dried material: S, 5·2; Br, 39·2. $C_{16}H_{10}O_5N_2Br_3SNa$ requires S, 5·3; Br, 39·6%).

1-*Hydroxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid* (IV).—A solution of the preceding sodium hydrogen salt (20 g.) in water (400 c.c.) was boiled, and concentrated hydrochloric acid (65 c.c.) added gradually until evolution of sulphur dioxide ceased and the *acid* (IV) separated in a granular condition (12 hours). It was washed with warm water and dried; it then crystallised from acetic acid in colourless prisms, m. p. 227—228° (12 g.; 66·6%) (Found : C, 36·9; H, 2·5; N, 5·3; Br, 46·1. $C_{16}H_{11}O_3N_2Br_3$ requires C, 37·0; H, 2·1; N, 5·4; Br, 46·2%). The *methyl* ester crystallised from methyl alcohol in colourless prisms, m. p. 172° (Found : C, 38·2; H, 2·6; N, 5·4. $C_{17}H_{13}O_3N_2Br_3$ requires C, 38·3; H, 2·4; N, 5·25%). The *N*-methyl ether, 1-*keto*-3-(2′ : 4′ : 6′-*tribromophenyl*)-2-*methyltetrahydrophthalazine*-4-*acetic acid*, crystallised from alcohol in small colourless prisms, m. p. 239—240° (Found : C, 38·5; H, 2·7; N, 4·95. $C_{17}H_{13}O_3N_2Br_3$ requires C, 38·3; H, 2·4; N, 5·25%). The *anilide* crystallised from acetic acid in colourless prisms, m. p. 266° (Found : loss at 135°, 16·6. $C_{22}H_{16}O_2N_3Br_3,2C_2H_4O_2$ requires $C_2H_4O_2$, 16·8%. Found in material heated at 135°; C, 44·2; H, 2·6; N, 7·0; Br, 39·9. $C_{22}H_{16}O_2N_3Br_3$ requires C, 44·4; H, 2·7; N, 7·1; Br, 40·4%). 1-*Acetoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid* crystallised from acetic acid in colourless prisms, m. p. 231—232° (decomp.) (Found : C, 38·6; H, 2·5; N, 4·6. $C_{18}H_{13}O_4N_2Br_3$ requires C, 38·5; H, 2·3; N, 5·0%).

2′ : 4′ : 6′-*Tribromo*-3-*phenylphthalaz*-1-*one*.—(*a*) A solution of 1-hydroxy-3-(2′ : 4′ : 6′-tribromophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (3·4 g.) in concentrated sulphuric acid (17 c.c.) and water (20 c.c.) was refluxed for 1·5 hours; the solution was diluted with water (30 c.c.) and filtered (charcoal); colourless needles of the sulphate then separated; these were collected and basified with sodium carbonate. The *phthalazone* crystallised from alcohol in colourless prismatic needles, m. p. 305° (decomp.) (2 g.; 66·6%) (Found : C, 37·0; H, 1·6; N, 6·1; Br, 52·5. $C_{14}H_7ON_2Br_3$ requires C, 36·6; H, 1·5; N, 6·1; Br, 52·3%), which turned blue on exposure to light. The *picrate* separated from

alcohol in bright yellow rectangular prisms, m. p. 266° (decomp.) (Found : C, 35·1; H, 1·8; Br, 34·3. $C_{20}H_{10}O_8N_5Br_3$ requires C, 34·9; H, 1·45; Br, 34·8%).

(*b*) 1-Hydroxy-3-(2′ : 4′ : 6′-tribromophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) was dissolved in concentrated sulphuric acid (50 c.c.), acetic acid (60 c.c.) added, and the solution refluxed gently for 15 minutes. On pouring on ice, the sulphate separated and was converted into the phthalazone (5·5 g.; 62·5%).

Action of Methyl Sulphate.—2′ : 4′ : 6′-Tribromo-3-phenylphthalaz-1-one (6 g.) was dissolved in nitrobenzene (120 c.c.), and the temperature gradually raised to 125°. Methyl sulphate (3 g.) was added, and, after 45 minutes at the same temperature, nitrobenzene was removed with steam and the aqueous residue was made alkaline with sodium carbonate. The almost colourless precipitate was washed with water and dried (5 g.). It crystallised from ethyl alcohol in small, almost colourless prisms, m. p. 135—136° (Found : C, 39·3; H, 2·9; N, 5·1; Br, 46·5. $C_{17}H_{15}O_2N_2Br_3$ requires C, 39·3; H, 2·9; N, 5·4; Br, 46·2%), or from methyl alcohol in larger, pale yellow prismatic needles, m. p. 138—139° (Found : C, 38·2; H, 2·6; N, 5·5. $C_{16}H_{13}O_2N_2Br_3$ requires C, 38·0; H, 2·6; N, 5·5%).

2′ : 4′-*Dibromo*-N-*phenylphthalimidine.*—A solution of the above phthalazone (2 g.) in water (20 c.c.), hydrochloric acid (50 c.c.), alcohol (20 c.c.), and acetic acid (20 c.c.) was heated with zinc amalgam (70 g.) at 90° for 5 hours. The mixture was cooled, filtered, and poured on ice; the *phthalimidine* crystallised from alcohol in colourless prisms, m. p. 126—127° (0·7 g.; 43·7%) (Found : C, 46·2; H, 2·4; N, 4·0; Br, 43·1. $C_{14}H_9ONBr_2$ requires C, 45·9; H, 2·2; N, 3·8; Br, 43·7%).

1 : 4-*Diketo*-3-(2′ : 4′ : 6′-*tribromophenyl*)*tetrahydrophthalazine* (IX).—Finely powdered potassium permanganate (15 g.) was added during 5 minutes to a suspension of 1-hydroxy-3-(2′ : 4′ : 6′-tribromophenyl)-3 : 4-dihydrophthalazine-4 -acetic acid (10 g.) in water (150 c.c.) at 70°. Reaction was vigorous, and the mixture was boiled and filtered hot; the yellow filtrate was cooled and acidified with hydrochloric acid. The *tetrahydrophthalazine* crystallised from acetic acid in small, colourless prismatic needles, m. p. 333—334° (6 g.; 63·2%) (Found : C, 35·7; H, 1·5; N, 5·6. $C_{14}H_7O_2N_2Br_3$ requires C, 35·4; H, 1·5; N, 5·9%). The *silver* salt (Found : Ag, 18·5. $C_{14}H_6O_2N_2Br_3Ag$ requires Ag, 18·5%) did not react with methyl iodide in dry benzene.

2′ : 4′ : 6′-*Tribromo*-3-*phenyl*-4-*methylphthalaz*-1-*one.*—(*a*) 1-Hydroxy-3-(2′ : 4′ : 6′-tribromophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) was dissolved in cold concentrated sulphuric acid (75 c.c.), and the solution poured on ice (250 g.). Finely powdered potassium dichromate (3 g.) was added, with stirring, during 2 hours, and the yellow precipitate of the sulphate of the phthalazone was collected and basified with warm aqueous ammonia. The *phthalazone* crystallised from alcohol in pale greenish prisms, melting at 150°, solidifying and remelting at 252° (6·6 g.; 72·5%) (Found : loss at 120°, 4·3. $C_{15}H_9ON_2Br_3,0{\cdot}5C_2H_6O$ requires C_2H_6O, 4·6%. Found in material heated at 120° : C, 37·9; H, 2·0; N, 5·6; Br, 50·4. $C_{15}H_9ON_2Br_3$ requires C, 38·0; H, 1·9; N, 5·9; Br, 50·7%). Its *picrate* crystallised from dry alcohol in yellow rhombs, m. p. 249° (Found : N, 10·1; Br, 34·1. $C_{21}H_{12}O_8N_3Br_3$ requires N, 10·0; Br, 34·1%).

(*b*) 1-Hydroxy-3-(2′ : 4′ : 6′-tribromophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (2 g.) was dissolved in nitric acid (*d* 1·51; 20 c.c.), and the solution heated at 50° for 4 minutes, poured on ice, and the precipitated nitrate collected and basified with warm aqueous ammonia. The product crystallised from ethyl acetate in colourless prisms, m. p. 252°, of 3-(2′ : 4′ : 6′-tribromophenyl)-4-methylphthalaz-1-one (1·1 g.; 48·8%).

1-*Methoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine.*—2′ : 4′ : 6′-Tribromo-3-phenyl-4-methylphthalaz-1-one (5·6 g.) was dissolved in dry nitrobenzene (40 c.c.) at 130°, and methyl sulphate (4 c.c.) added. The solution was left for 1 hour at the same temperature, nitrobenzene removed with steam, the aqueous residue filtered from a little resin, and the filtrate made alkaline with sodium carbonate solution. The *methylene base* crystallised from alcohols, but better from ethyl acetate, in pale yellow, prismatic needles, m. p. 153° (3 g.; 63·3%) (Found : C, 39·1; H, 2·7; N, 5·9; Br, 48·7. $C_{16}H_{11}ON_2Br_3$ requires C, 39·4; H, 2·3; N, 5·75; Br, 49·2%), readily soluble in dilute mineral acids to give colourless solutions. Addition of 60% perchloric acid (10 c.c.) to the methylene derivative (1 g.) in hydrochloric acid (5 c.c.) and water (30 c.c.) gave the *perchlorate*, which crystallised from alcohol containing a trace of perchloric acid, in colourless prisms, m. p. 230° (Found : C, 33·05; H, 2·0; 4·755 mg. gave 5·68 mg. AgCl + AgBr. $C_{16}H_{11}O_5N_2ClBr_3$ requires C, 32·7; H, 1·7%; AgCl + AgBr, 5·735 mg.), decomposed by aqueous alkalis to give the base.

1-*Methoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-4-(5′′-*keto*-1′′-*phenyl*-3′′-*methylpyrazolinylidene*-*ethylidene*)-3 : 4-*dihydrophthalazine.*—A solution of 1-methoxy-3-(2′ : 4′ : 6′-tribromophenyl)-4-methylene-3 : 4-dihydrophthalazine (1 g.) and 1-phenyl-3-methyl-4-anilinomethylene-5-pyrazolone (1 g.) in acetic anhydride (5 c.c.) and acetic acid (6 c.c.) was heated at 100° for 9 hours. The *compound* crystallised from acetic anhydride in greenish-black prisms, m. p. 224° (0·6 g.; 44%) (Found : N, 8·3. $C_{27}H_{19}O_2N_4Br_3$ requires N, 8·3%).

1-*Methoxy*-3-(2′ : 4′ : 6′-*tribromophenyl*)-4-(2′′ : 4′′-*dinitrobenzylidene*)-3 : 4-*dihydrophthalazine.*—2 : 4-Dinitrochlorobenzene (1·2 g.) was added to a suspension of 1-methoxy-3-(2′ : 4′ : 6′-tribromophenyl)-4-methylene-3 : 4-dihydrophthalazine (2 g.) in hot alcohol (60 c.c.), and the mixture refluxed for 4 hours. A deep red colour developed rapidly, and concentration to 50 c.c., followed by cooling at 0°, gave a tar which slowly solidified; the *compound* was crystallised several times from alcohol; it separated in dark red needles, m. p. 138—140° (0·6 g.; 23%) (Found : C, 40·6; H, 2·1; N, 8·1. $C_{22}H_{13}O_5N_4Br_3$ requires C, 40·4; H, 2·0; N, 8·5%), soluble in concentrated sulphuric acid with a yellow colour.

o-*Carboxybenzaldehyde* 2′ : 4′ : 6′-*Tribromophenylhydrazone.*—2 : 4 : 6-Tribromophenylhydrazine (3·7 g.) was dissolved in cold benzene (400 c.c.) and the solution added to a solution of *o*-phthalaldehydic acid (1·5 g.) in cold benzene (400 c.c.). After 2 hours, the *carboxy*-derivative had separated in colourless needles, m. p. 204° (2·7 g.; 51·7%) (Found : C, 35·5; H, 1·9; N, 6·0; Br, 50·8. $C_{14}H_9O_2N_2Br_3$ requires C, 35·2; H, 5·8; N, 5·8; Br, 50·3%).

2′ : 4′ : 6′-*Tribromo*-3-*phenylphthalaz*-4-*one.*—*o*-Carboxybenzaldehyde 2′ : 4′ : 6′-tribromophenylhydrazone (2 g.) was dissolved in amyl alcohol (20 c.c.), and the solution saturated with dry hydrogen

chloride. The solution was then refluxed for 1 hour, and the *phthalazone* collected; it crystallised from acetic acid in small colourless prisms, m. p. 182° (0·8 g.; 40·8%) (Found: C, 36·9; H, 1·6; N, 5·8; Br, 52·3. $C_{14}H_7ON_2Br_3$ requires C, 36·7; H, 1·5; N, 6·1; Br, 52·3%), insoluble in mineral acids and aqueous alkalis. It was obtained also by heating 3-(2′ : 4′ : 6′-tribromophenyl)phthalaz-1-one (1·4 g.) with aqueous hydrochloric acid (1 : 8; 18 c.c.) at 190—200° for 64 hours (0·1 g.; 7%).

o-Carboxyacetophenone 2′ : 4′ : 6′-Tribromophenylhydrazone.—A solution of acetophenone-*o*-carboxylic acid (2 g.) in boiling alcohol (10 c.c.) was added to a solution of 2 : 4 : 6-tribromophenylhydrazine (3 g.) in alcohol (80 c.c.). On standing, the *hydrazone* separated progressively in almost colourless needles, needles, m. p. 171° (3 g.; 71·4%) (Found: C, 37·15; H, 2·4; N, 5·7; Br, 49·3. $C_{15}H_{11}O_2N_2Br_3$ requires C, 36·6; H, 2·2; N, 5·7; Br, 48·8%), soluble in cold aqueous alkalis.

2′ : 4′ : 6′-Tribromo-3-phenyl-1-methylphthalaz-4-one.—*o*-Carboxyacetophenone 2′ : 4′ : 6′-tribromophenylhydrazone (2 g.) was refluxed with acetic acid (40 c.c.) for 3 hours; on cooling, the *phthalazone* separated in colourless needles, m. p. 195° (1·2 g.; 61·2%) (Found: C, 37·7; H, 2·2; N, 5·6. $C_{15}H_9ON_2Br_3$ requires C, 38·0; H, 1·9; N, 5·9%), insoluble in mineral acids and alkalis. It was also obtained in low yield by heating the isomeric 4-methylphthalaz-1-one with aqueous hydrochloric acid (1 : 8) in a sealed tube at 190—200° for 52 hours.

Sodium Hydrogen 3-(3′-Chlorophenyl)-3 : 4-dihydrophthalazine-1-sulphonate-4-acetate.—The *salt* was prepared in an analogous manner to that given for the 2′ : 4′ : 6′-tribromo-derivative; it was precipitated by ether from a solution in ethyl acetate as a yellow solid (55% yield) (Found: S, 6·6. $C_{16}H_{12}O_5N_2SClNa$ requires S, 7·9%).

1-Hydroxy-3-(3′-chlorophenyl)-3 : 4-dihydrophthalazine-4-acetic Acid.—This was obtained in 26% yield by hydrolysis of the above sodium salt; it crystallised from acetic acid in colourless prisms, m. p. 200° (Found: C, 60·6; H, 3·9; N, 8·9; Cl, 11·3. $C_{16}H_{13}O_3N_2Cl$ requires C, 60·75; H, 4·1; N, 8·9; Cl, 11·0%). The *methyl* ester crystallised from methyl alcohol in minute, colourless prisms, m. p. 123° (Found: C, 61·9; H, 4·6; N, 8·6. $C_{17}H_{15}O_3N_2Cl$ requires C, 61·7; H, 4·55; N, 8·5%). The N-*methyl ether* crystallised from alcohol in colourless prisms, m. p. 197° (Found: N, 8·55; Cl, 10·7. $C_{17}H_{15}O_3N_2Cl$ requires N, 8·5; Cl, 10·7%). The *anilide* crystallised from toluene in clusters of small yellow needles, m. p. 173—175° (Found: N, 10·5; Cl, 9·0. $C_{22}H_{18}O_3N_3Cl$ requires N, 10·7; Cl, 9·0%). *1-Acetoxy-3-(3′-chlorophenyl)-3 : 4-dihydrophthalazine-4-acetic acid* crystallised from acetic acid in colourless prisms, m. p. 175—176° (Found: N, 8·0; Cl, 9·7. $C_{18}H_{15}O_4N_2Cl$ requires N, 7·8; Cl, 9·9%), soluble in cold aqueous sodium carbonate with a yellow colour.

3′-Chloro-3-phenylphthalaz-1-one.—1-Hydroxy-3-(3′-chlorophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (4 g.) was refluxed with concentrated sulphuric acid (30 c.c.) and water (35 c.c.) for 3 hours. The *phthalazone*, isolated in the usual manner, crystallised from alcohol in colourless prisms, m. p. 278° (2·5 g.; 78·1%) (Found: C, 65·0; H, 3·7; N, 10·7; Cl, 14·1. $C_{14}H_9ON_2Cl$ requires C, 65·5; H, 3·5; N, 10·9; Cl, 13·8%). It gave a *picrate*, minute yellow plates, m. p. 253—254° (Found: N, 14·1. $C_{20}H_{12}O_8N_5Cl$ requires N, 14·4%).

3′-Chloro-N-phenylphthalimidine.—3′-Chloro-3-phenylphthalaz-1-one (1 g.) was dissolved in hydrochloric acid (20 c.c.), water (10 c.c.), alcohol (10 c.c.), and acetic acid (20 c.c.), and the solution was warmed with zinc amalgam (30 g.) at 75° for 2 hours. The *phthalimidine* crystallised from alcohol in colourless needles, m. p. 185° (0·4 g.; 84%) (Found: C, 69·3; H, 4·0; N, 6·0; Cl, 14·6. $C_{14}H_{10}ONCl$ requires C, 68·9; H, 4·0; N, 5·75; Cl, 14·9%).

3′-Chloro-3-phenyl-4-methylphthalaz-1-one Sulphate.—1-Hydroxy-3-(3′-chlorophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (15 g.) was dissolved in concentrated sulphuric acid (120 c.c.) and poured on ice (300 g.). Finely powdered potassium dichromate (8 g.) was added gradually with cooling. The green solution was stirred for 3 hours at room temperature and then neutralised with aqueous sodium hydroxide. Extraction of the precipitate with aqueous alcohol gave a solid which crystallised with difficulty from the same solvent in colourless cubes, m. p. 320°, of the *sulphate* (9·5 g.; 64·6%) (Found: C, 47·9; H, 3·8; Cl, 9·5. $C_{15}H_{13}O_5N_2ClS$ requires C, 48·8; H, 3·5; Cl, 9·5%). Basification with ammonia or sodium carbonate or hydroxide gave only an intractable tar, which yielded a *picrate*, yellow needles, m. p. 219° (Found: N, 13·8. $C_{21}H_{14}O_8N_5Cl$ requires N, 14·0%).

1-Keto-3-(3′-chlorophenyl)-4-methyltetrahydrophthalazine (VI).—3′-Chloro-3-phenyl-4-methylphthalaz-1-one sulphate (1 g.) was warmed with hydrochloric acid (20 c.c.), water (20 c.c.), alcohol (10 c.c.), and acetic acid (7 c.c.). The temperature was raised to 90°, and zinc amalgam (60 g.) added, and after 3 hours at the same temperature the mixture was poured on ice; the precipitate of *tetrahydrophthalazine* crystallised from alcohol in colourless rhombs, m. p. 178° (0·5 g.; 50%) (Found: C, 66·1; H, 4·6; Cl, 12·6. $C_{15}H_{13}ON_2Cl$ requires C, 66·05; H, 4·8; Cl, 13·0%).

1 : 4-Diketo-3-(3′-chlorophenyl)tetrahydrophthalazine.—A suspension of 1-hydroxy-3-(3′-chlorophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (5 g.) in water (100 c.c.) was treated with potassium permanganate (8 g.) at 70° during 5 minutes. The reaction was vigorous, and, after it had subsided, the mixture was boiled for 5 minutes and filtered, and the filtrate was acidified; the *tetrahydrophthalazine* crystallised from aqueous alcohol in almost colourless prisms, m. p. 226—230° (0·85 g.; 19·7%) (Found: C, 60·9; H, 3·7; N, 10·1. $C_{14}H_9O_2N_2Cl$ requires C, 61·2; H, 3·3; N, 10·2%), soluble in cold aqueous ammonia with a yellow colour.

3′-Chloro-3-phenylphthalaz-4-one.—A solution of *m*-chlorophenylhydrazine (2 g.) in alcohol (8 c.c.) was refluxed with a solution of *o*-phthalaldehydic acid (2 g.) in alcohol (12 c.c.) for 1 hour. The *phthalazone* crystallised from alcohol in colourless needles, m. p. 135° (yield, 1·5 g.; 41·6%) (Found: C, 65·8; H, 3·5; N, 10·9; Cl, 13·95. $C_{14}H_9ON_2Cl$ requires C, 65·5; H, 3·5; N, 10·9; Cl, 13·8%). It is insoluble in mineral acids and alkalis and does not form a picrate. It was also obtained in 71% yield by heating the isomeric phthalaz-1-one with aqueous hydrochloric acid (1 : 8) at 200° in a sealed tube for 60 hours.

3′-Chloro-3-phenyl-1-methylphthalaz-4-one.—Alcoholic solutions of *m*-chlorophenylhydrazine (1·4 g. in 10 c.c.) and acetophenone-*o*-carboxylic acid (1·4 g. in 10 c.c.) were mixed cold and then refluxed for 20 minutes. The *compound* separated in clusters of colourless needles, m. p. 140° (1·3 g.; 50%) (Found: C, 66·6; H, 4·1; N, 10·2. $C_{15}H_{11}ON_2Cl$ requires C, 66·5; H, 4·0; N, 10·3%), insoluble in acids or

alkalis. A 60% conversion of the isomeric 4-methyl-1-one into the 1-methyl-4-one was effected by aqueous hydrochloric acid (1 : 8) at 200° in a sealed tube for 55 hours.

Sodium Hydrogen 3-(4′-*Chlorophenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*.—This was isolated in the usual manner, but was resinous (Found : N, 5·3. $C_{16}H_{12}O_5N_2SClNa$ requires N, 6·9%).

1-*Hydroxy*-3-(4′-*chlorophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid*.—Hydrolysis of the above salt yielded the *hydroxy*-compound, which crystallised from acetic acid in colourless needles, m. p. 236° (Found : N, 9·2; Cl, 10·8. $C_{16}H_{13}O_3N_2Cl$ requires N, 8·9; Cl, 11·0%).

4′-*Chloro*-3-*phenylphthalaz*-1-*one*.—A solution of the above hydroxy- compound (10 g.) in concentrated sulphuric acid (70 c.c.) and water (84 c.c.) was refluxed for 2 hours. The *phthalaz*-1-*one* separated from alcohol in colourless needles, m, p. 281—283° (3·6 g.; 44·4%) (Found : C, 65·3; H, 3·7; N, 10·6; Cl, 14·2. $C_{14}H_9ON_2Cl$ requires C, 65·5; H, 3·5; N, 10·9; Cl, 13·8%).

4′-*Chloro*-N-*phenylphthalimidine*.—Prepared as for the 3′-chloro-analogue, this *compound* crystallised from alcohol in colourless, hexagonal plates, m. p. 180° (Found : C, 68·9; H, 4·0. $C_{14}H_{10}ONCl$ requires C, 68·9; H, 4·0%).

4′-*Chloro*-3-*phenyl*-4-*methylphthalaz*-1-*one* (VII).—This crystallised from alcohol in colourless, prismatic needles, shrinking at 220° and melting at 238°, turning green in air; the *picrate* separated from dry alcohol in yellow rectangular prisms, m. p. 200° (Found : N, 14·1. $C_{21}H_{14}O_8N_5Cl$ requires N, 14·0%).

4′-*Chloro*-N-*phenyl*-3-*methylphthalimidine* (VIII).—4′-Chloro-3-phenyl-4-methylphthalaz-1-one (1 g.) was refluxed with zinc amalgam (35 g.) in hydrochloric acid (20 c.c.), alcohol (10 c.c.), acetic acid (10 c.c.) and water (10 c.c.) for 3 hours. The *phthalimidine* crystallised from alcohol in colourless prismatic needles, m. p. 185° (0·5 g.; 71%) (Found : C, 70·2; H, 4·3. $C_{15}H_{12}ONCl$ requires C, 69·9; H, 4·6%).

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

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