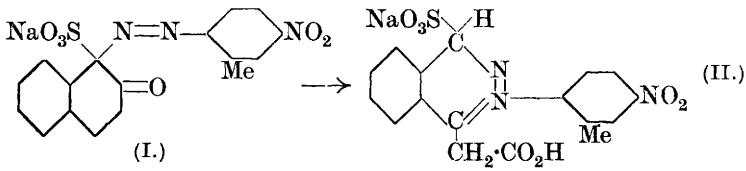
56. *A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part IX. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from 5-Nitro-o-toluidine.*

By Frederick Maurice Rowe and Francis Joseph Siddle.

In order to obtain further evidence with regard to the constitutions attributed to the phthalazine, phthalazone and phthalimidine derivatives prepared from β-naphthol-1-sulphonic acid and diazotised *p*-nitroaniline (J., 1926, 690; 1928, 2550; 1931, 1067), the compounds now described from 5-nitro-*o*-toluidine were examined at the same time as those prepared from the halogen derivatives (J., 1931, 1073; this vol., p. 11).

In general, the course of the reactions and the properties and yields of the products in the present series approximate to those observed with the analogous lower homologues containing the nitro- or amino-group in the 4′-position, but in some instances the 2′-methyl group leads to similar results to those obtained with compounds containing a 2′-chloro-atom.

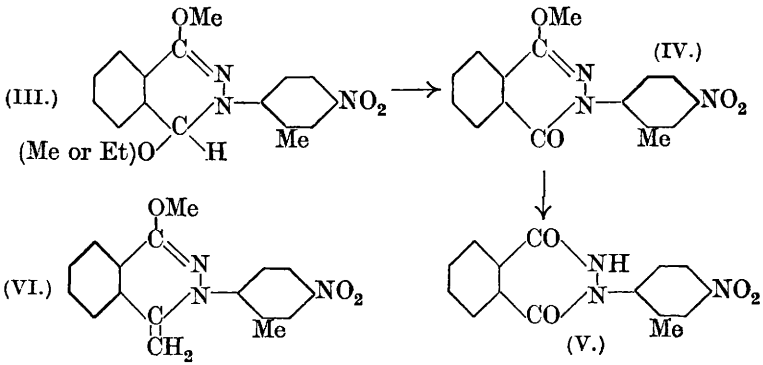
Conversion of 4′-nitro-2′-methylbenzene-2-naphthol-1-diazosulphonate through sodium 1-(4′-nitro-2′-methylbenzeneazo)-β-naphthaquinone-1-sulphonate (I) into *sodium hydrogen* 3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (II) proceeds readily and little 4′-nitro-2′-methylbenzeneazo-β-naphthol is formed.



The sodium hydrogen salt possesses greater tinctorial power than the analogous lower homologue, but is also fugitive to light. In replacing the sodium-1-sulphonate group by hydroxyl, the use of too concentrated acid precipitates the free sulphonic acid, which is then hydrolysed only with difficulty. 1-*Hydroxy*-3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*, however, is obtained readily by the use of more dilute acid and this modification appears to be generally applicable. Reduction to 1-*hydroxy*-3-(4′-*amino*-2′-*methylphenyl*)*tetrahydrophthalazine*-4-*acetic acid* can be effected either with alkaline hydrosulphite (hyposulphite) or with stannous chloride and hydrochloric acid, but the former is the better

method, as subsequent degradation is more rapid with acid than with alkali.

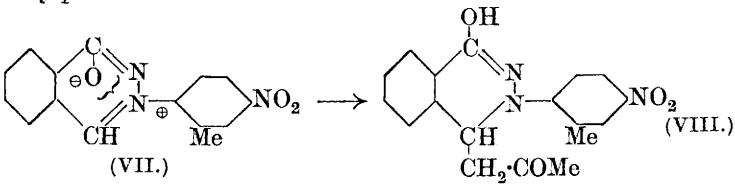
Unexpected difficulties were encountered in preparing 2′-chloro-4′-nitro-3-phenylphthalaz-1-one (*loc. cit.*), but 4′-*nitro*-3-*phenyl*-2′-*methylphthalaz*-1-*one* (VII) and its 4-*methyl* derivative respectively are formed from 1-hydroxy-3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-4-acetic acid in the usual manner. Methylation of the oxygen atom in the keto-group of 4′-nitro-3-phenyl-2′-methylphthalaz-1-one proceeds similarly to the case of the analogous lower homologue. The primary product combines with alcohols (III) and is then so reactive that it is impossible to determine its formula by analysis. By heating the compound after crystallisation from an alcohol first at 100° and then at 140°, however, it is converted into 4-*keto*-1-*methoxy*-3-(4′-*nitro*-2′-*methylphenyl*)-3 : 4-*dihydrophthalazine* (IV), from which 1 : 4-*diketo*-3-(4′-*nitro*-2′-*methylphenyl*)*tetrahydrophthalazine* (V) is obtained by demethylation.



This behaviour, therefore, is quite different from that of the dihalogeno-derivatives (*loc. cit.*). On the other hand, the methylation of 4′-nitro-3-phenyl-2′ : 4-dimethylphthalaz-1-one is comparable with all other cases yet examined and gives 4′-*nitro*-1-*methoxy*-3-*phenyl*-2′-*methyl*-4-*methylene*-3 : 4-*dihydrophthalazine* (VI).

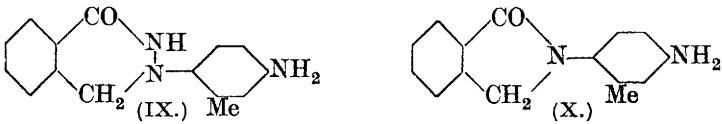
In view of the properties of the nitro-3-phenylphthalaz-1-ones, it appeared possible that they might react with acetone in a similar manner to berberine (compare Pyman, J., 1911, **99**, 1690). 4′-Nitro-3-phenyl-2′-methylphthalaz-1-one (VII) does react with acetone, but differs from berberine in that the final result is equivalent to the addition of acetone, and 1-*hydroxy*-4-*acetonyl*-3-(4′-*nitro*-2′-*methylphenyl*)-3 : 4-*dihydrophthalazine* (VIII) is formed. This behaviour, however, is unique at present in that we have failed

to prepare corresponding acetone compounds from any other nitro-3-phenylphthalaz-1-ones.



(VII.) (VIII.)

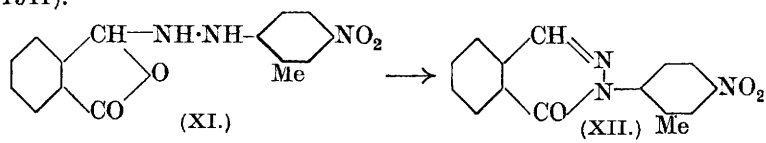
1-Hydroxy-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine-4-acetic acid is converted into 4′-*amino*-3-*phenyl*-2′-*methylphthalaz*-1-*one* and its 4-*methyl* derivative respectively in the usual manner, the latter being formed even by heating with sodium carbonate solution at the ordinary pressure. The products obtained by reduction of these amino-3-phenylphthalaz-1-ones vary with the conditions employed. Thus, reduction with alkaline hydrosulphite gives 1-*keto*-3-(4′-*amino*-2′-*methylphenyl*)*tetrahydrophthalazine* (IX) and its 4-*methyl* derivative respectively, whereas reduction with zinc dust and hydrochloric acid gives 4′-*amino*-N-*phenyl*-2′-*methylphthalimidine* (X) and its 3-*methyl* derivative respectively.



(IX.) (X.)

In the latter cases decomposition also always occurs with formation of some *p*-tolylenediamine.

Finally, 4′-*nitro*-3-*phenyl*-2′-*methylphthalaz*-4-*one* (XII) was prepared for purposes of comparison. The condensation of equimolecular proportions of phthalaldehydic acid and 5-nitro-*o*-tolylhydrazine in boiling alcoholic solution gives the *lactone* form of o-*carboxybenzaldehyde*-5-*nitro*-o-*tolylhydrazone* (XI), which is much more stable than the analogous lower homologue (*loc. cit.*). A molecule of water is eliminated, however, when the hydrazone is dissolved in warm concentrated sulphuric acid or in amyl-alcoholic hydrogen chloride (compare Aggarwal, Darbari, and Rây, J., 1929, 1941).



(XI.) (XII.)

4′-Nitro-3-phenyl-2′-methylphthalaz-4-one does not form salts with mineral acids or with picric acid, is insoluble in sodium hydroxide solution, and does not react with methyl sulphate.

Work on the action of sodium hydroxide on various 2′-nitrobenzene-2-naphthol-1-diazosulphonates, which exhibit striking differences from the 3′- and 4′-nitro-isomerides, is in progress.

EXPERIMENTAL.

Where details are omitted, the compounds were prepared by exactly the same procedure as that described for the corresponding lower homologues containing the nitro- or amino-group in the 4′-position (J., 1926, 699; 1928, 2553; 1931, 1070).

Sodium Hydrogen 3-(4′-*Nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (II).—A filtered solution of commercial 50% sodium β-naphthol-1-sulphonate (50 g.) in water (170 c.c.) was stirred slowly at 0° into a solution of diazotised 5-nitro-*o*-toluidine. The latter was obtained by adding a concentrated aqueous solution of sodium nitrite (7·3 g.) to a suspension of the base (15·2 g.) in dilute hydrochloric acid (190 c.c. of 1 : 5). The 4′-nitro-2′-methylbenzene-2-naphthol-1-diazosulphonate separated immediately as an orange precipitate, which was filtered off, washed free from acid with water, made into a paste with cold water (160 c.c.), and stirred into a cold solution of anhydrous sodium carbonate (28 g.) in water (70 c.c.). The orange solution produced [orange needles of sodium 1-(4′-nitro-2′-methylbenzeneazo)-β-naphthaquinone-1-sulphonate (I) separated on addition of salt] was added immediately to a cold solution of sodium hydroxide (25 g.) in water (45 c.c.); the temperature rose about 8°, and the deep crimson mixture was left overnight until the colour had changed completely to yellowish-brown. The pure product was isolated in the usual manner, after separation from 4′-nitro-2′-methylbenzeneazo-β-naphthol (1—2 g.). *Sodium hydrogen* 3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (yield, 37 g.; 86·7%, calculated on the 5-nitro-*o*-toluidine) crystallised from alcohol in large, orange, irregular prisms (Found: S, 7·8. $C_{17}H_{14}O_7N_3SNa$ requires S, 7·5%). It was readily soluble in water, but less soluble in alcohol. The yellow aqueous solution was deepened in colour by the addition of alkali, and was decolorised by zinc dust and ammonia, a deeper colour returning on exposure to air. It is a level-dyeing, yellow acid dye of even greater tinctorial power than the lower homologue, but also fugitive to light.

1-*Hydroxy*-3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—A solution of sodium hydrogen 3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-1-sulphonate-4-acetate (60 g.) in water (250 c.c.) was boiled, and concentrated hydrochloric acid (30 c.c.) added gradually (to avoid precipitation of the free sulphonic acid) until evolution of sulphur dioxide had ceased and the product

had formed a straw-coloured crystalline mass. The latter was washed with boiling water and crystallised from ethyl acetate. 1-*Hydroxy*-3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* formed pale yellow plates, m. p. 238° (yield, 44 g.; 91·8%) (Found: C, 59·95; H, 4·6; N, 12·5. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%), readily soluble in alcohol, acetone or glacial acetic acid, but almost insoluble in benzene and toluene, and insoluble in ether. It was very sparingly soluble in water, forming a solution acid to litmus, but dissolved in sodium carbonate or hydroxide with a deep red colour, and in cold concentrated sulphuric acid with an orange colour, being reprecipitated unaltered on dilution.

Derivatives of 1-*Hydroxy*-3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—The *methyl* ester crystallised from methyl alcohol in pale yellow, rhombic prisms, m. p. 186° (Found: C, 61·05; H, 4·8. $C_{18}H_{17}O_5N_3$ requires C, 60·85; H, 4·8%). The *ethyl* ester crystallised from alcohol in pale yellow, cubic prisms, m. p. 165° (Found: C, 61·95; H, 5·3. $C_{19}H_{19}O_5N_3$ requires C, 61·8; H, 5·15%). Both esters were insoluble in sodium carbonate solution, but dissolved in sodium hydroxide with a deep red colour. The *acetyl* derivative crystallised from alcohol in pale yellow needles, m. p. 228° (Found: C, 59·45; H, 4·7. $C_{19}H_{17}O_6N_3$ requires C, 59·5; H, 4·4%). It dissolved in sodium carbonate with an orange-brown colour and in sodium hydroxide with a blood-red colour. The *anilide* crystallised from ethyl acetate in yellow prisms, m. p. 211—212° (Found: C, 66·5; H, 4·9. $C_{23}H_{20}O_4N_4$ requires C, 66·3; H, 4·8%). It was soluble in warm sodium hydroxide solution with a brownish-red colour.

1-*Hydroxy*-3-(4′-*amino*-2′-*methylphenyl*)*tetrahydrophthalazine*-4-*acetic Acid*.—Prepared from 1-hydroxy-3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-4-acetic acid (12 g.) by reduction with alkaline sodium hydrosulphite (pale yellow prisms of the sodium salt separated incompletely from the cold reduction mixture); this *acid* crystallised from a large volume of boiling water in colourless prisms, m. p. 217° (yield, 10·6 g.; 96·2%) (Found: C, 65·2; H, 5·9; N, 13·6. $C_{17}H_{19}O_3N_3$ requires C, 65·2; H, 6·1; N, 13·4%). It was prepared also by rapid reduction of 1-hydroxy-3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-4-acetic acid (10 g.) with boiling acid stannous chloride (40 g. in 100 c.c. of concentrated hydrochloric acid), and was isolated by rendering the solution alkaline with sodium carbonate, filtering it, and precipitating the filtrate with acid (yield, 7·5 g.; 81·7%). It dissolved in alcohol and glacial acetic acid, but crystallisation from these solvents lowered the melting point, probably owing to partial esterification and acetylation respectively. It gave a transient red colour with

ferric chloride. The *acetyl* derivative crystallised from glacial acetic acid in colourless needles, m. p. 265° (Found: C, 64·3; H, 6·0. $C_{19}H_{21}O_4N_3$ requires C, 64·2; H, 5·9%).

4′-Amino-3-phenyl-2′-methylphthalaz-1-one.—A solution of 1-hydroxy-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine-4-acetic acid (5 g.) in concentrated sulphuric acid (25 c.c.) and water (30 c.c.) was boiled under reflux for 1½ hours, acetic acid being eliminated. The solution was diluted with water (50 c.c.), boiled (charcoal), and filtered. The pale yellow solution was neutralised with sodium hydroxide solution; long yellow needles then separated, m. p. 130°, containing water of crystallisation, or m. p. 249—251°, after drying at 120° (Found: loss at 120°, 3·55. $C_{15}H_{13}ON_3,\frac{1}{2}H_2O$ requires H_2O, 3·45%). *4′-Amino-3-phenyl-2′-methylphthalaz-1-one* crystallised from alcohol in yellow prisms, m. p. 255° (yield, 3·6 g.; 89·8%) (Found: C, 71·7; H, 5·4; N, 16·5. $C_{15}H_{13}ON_3$ requires C, 71·7; H, 5·2; N, 16·7%). It was prepared also (yield, 74·8%) by boiling a solution of 1-hydroxy-3-(4′-amino-2′-methylphenyl)-tetrahydrophthalazine-4-acetic acid in excess concentrated hydrochloric acid under reflux for 20 hours and then collecting the colourless needles of the hydrochloride after cooling. The *acetyl* derivative crystallised from alcohol in colourless rhomboidal plates, m. p. 300—302° (Found: C, 69·8; H, 5·3. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1%), which became blue on the surface on exposure to light.

1-Keto-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine (IX).—A fine suspension of 4′-amino-3-phenyl-2′-methylphthalaz-1-one (4 g.), obtained as described for the 2′-chloro-analogue (this vol., p. 16), was reduced similarly with alkaline sodium hydrosulphite until a paler yellow flocculent precipitate was obtained. *1-Keto-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine* crystallised from toluene in yellow needles, m. p. 203—205° (yield, 2·6 g.; 64·5%) (Found: C, 71·3; H, 6·15. $C_{15}H_{15}ON_3$ requires C, 71·15; H, 5·9%). Prolonged boiling with mineral acid or nitrobenzene resulted in partial reconversion into 4′-amino-3-phenyl-2′-methylphthalaz-1-one. The *acetyl* derivative crystallised from a large volume of toluene in pale yellow prisms, m. p. 212—214° (Found: C, 69·3; H, 6·0. $C_{17}H_{17}O_2N_3$ requires C, 69·15; H, 5·75%).

4′-Amino-N-phenyl-2′-methylphthalimidine (X).—This was prepared from 4′-amino-3-phenyl-2′-methylphthalaz-1-one (5 g.). The hydrochloride did not separate and the product was precipitated by adding excess of sodium hydroxide to the reduction mixture. The filtrate contained ammonia and some *p*-tolylenediamine. *4′-Amino-N-phenyl-2′-methylphthalimidine* crystallised from alcohol in colourless flat prisms, m. p. 176—177° (yield, 3 g.; 63·3%) (Found: C,

75·7; H, 5·9. $C_{15}H_{14}ON_2$ requires C, 75·6; H, 5·9%). The hydrochloride formed colourless plates and the *acetyl* derivative crystallised from alcohol in colourless prismatic needles, m. p. 185° (Found: C, 72·8; H, 5·95. $C_{17}H_{16}O_2N_2$ requires C, 72·9; H, 5·7%.)

4′-Hydroxy-N-phenyl-2′-methylphthalimidine was prepared from 4′-amino-*N*-phenyl-2′-methylphthalimidine. It crystallised from alcohol in colourless transparent prisms, m. p. 227° (Found: C, 75·4; H, 5·6. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4%). The *methyl* ether crystallised from methyl alcohol in colourless, flat, rectangular prisms, m. p. 161° (Found: C, 75·8; H, 6·15. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9%).

4′-Nitro-3-phenyl-2′-methylphthalaz-1-one (VII).—After 1-hydroxy-3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-4-acetic acid (5 g.) had been boiled with aqueous sulphuric acid (110 c.c.; b. p. 140°), the solution was diluted with water (50 c.c.), boiled (charcoal), and filtered. After cooling, the sulphate (colourless needles, m. p. 244–246°, resolidifying and then melting at 279°) was filtered off and neutralised with sodium carbonate. A further quantity, but less pure, was isolated by almost neutralising the filtrate. *4′-Nitro-3-phenyl-2′-methylphthalaz-1-one* crystallised from pyridine in light yellow needles, m. p. 279° (yield, 3 g.; 72·8%) (Found: C, 64·1; H, 4·1. $C_{15}H_{11}O_3N_3$ requires C, 64·1; H, 3·9%), readily soluble in glacial acetic acid, soluble in alcohol and nitrobenzene, and very sparingly soluble in benzene. It is insoluble in sodium carbonate, but dissolves in sodium hydroxide with a deep orange-red colour; with mineral acids it forms salts (the hydrochloride crystallised from alcohol in pale yellow needles, m. p. 195—199°, resolidifying and then melting at 279°), which are decomposed by water, although more stable than the salts of the lower homologue. With an alcoholic solution of picric acid it forms a *picrate*, bright yellow needles, m. p. 208—210°, decomposed progressively by recrystallisation from alcohol (Found: C, 49·6; H, 2·85. $C_{21}H_{14}O_{10}N_6$ requires C, 49·4; H, 2·75%).

Reduction. (a) A fine aqueous suspension of 4′-nitro-3-phenyl-2′-methylphthalaz-1-one was heated to 80° with aqueous sodium sulphide, and the orange-red solution was then boiled for 10 minutes until the colour had changed to brownish-yellow. The 4′-amino-3-phenyl-2′-methylphthalaz-1-one separated, identical with that obtained from 1-hydroxy-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine-4-acetic acid (p. 478).

(b) Reduction with zinc dust and hydrochloric acid converted the nitro-compound into 4′-amino-*N*-phenyl-2′-methylphthalimidine, identical with that obtained similarly from 4′-amino-3-phenyl-2′-methylphthalaz-1-one (p. 478).

Action of Methyl Sulphate on 4′-Nitro-3-phenyl-2′-methylphthalaz-1-one.—An orange-yellow substance was obtained, which formed a hydrochloride, colourless needles, and was insoluble in cold alkalis. The basic substance could not be crystallised from ethyl acetate, but with alcohol became first resinous and then crystalline (III). Thus crystallisation from ethyl alcohol gave orange leaflets, m. p. 93°, and crystallisation from methyl alcohol gave orange leaflets, m. p. 149—150°. The latter compounds decomposed on drying and so could not be analysed, but by heating first at 100° and then at 140° both were converted gradually into 4-keto-1-methoxy-3-(4′-nitro-2′-methylphenyl)-3 : 4-dihydrophthalazine (IV). There was also formed simultaneously a certain amount of a second substance, red prisms, m. p. 255°, especially if heating was too rapid at first (compare J., 1928, 2562).

4-Keto-1-methoxy-3-(4′-nitro-2′-methylphenyl)-3 : 4-dihydrophthalazine crystallised from alcohol in pale yellow needles or from glacial acetic acid in colourless needles, m. p. 184—185° (Found: C, 61·8; H, 4·3; N, 13·6; OMe, 9·9. $C_{16}H_{13}O_4N_3$ requires C, 61·7; H, 4·2; N, 13·5; OMe, 10·0%). Hydrobromic acid converted it into *1 : 4-diketo-3-(4′-nitro-2′-methylphenyl)tetrahydrophthalazine* (V), which crystallised from glacial acetic acid in almost colourless needles, m. p. 267° (Found: C, 60·3; H, 3·9. $C_{15}H_{11}O_4N_3$ requires C, 60·2; H, 3·7%), insoluble in dilute mineral acids, but soluble in dilute sodium carbonate with a yellow colour.

Action of acetone. 4′-Nitro-3-phenyl-2′-methylphthalaz-1-one (2 g.) was converted into the sulphate, which was dissolved in the minimum amount of dilute sulphuric acid (1 : 3) at 80°. One-half the volume of acetone was added to the hot solution and after 5 minutes the mixture was rendered just alkaline with aqueous sodium hydroxide. After the deep red solution had been cooled, the white precipitate was collected, washed well with water, and dried. *1-Hydroxy-4-acetonyl-3-(4′-nitro-2′-methylphenyl)-3 : 4-dihydrophthalazine* (VIII) crystallised from acetone in colourless needles, m. p. 186—187° (yield, 1·4 g.; 58%) (Found: C, 63·9; H, 5·1; N, 12·2. $C_{18}H_{17}O_4N_3$ requires C, 63·7; H, 5·0; N, 12·4%), insoluble in cold sodium carbonate, but soluble in sodium hydroxide solution with an orange-red colour. Unlike berberine-acetone (compare Gaze, *Z. Naturwiss. Halle*, 1890, **62**, 399), it was unaltered when its alcoholic solution was boiled with chloroform.

4′-Nitro-3-phenyl-2′ : 4-dimethylphthalaz-1-one.—A solution of 1-hydroxy-3-(4′-nitro-2′-methylphenyl)-1 : 3-dihydrophthalazine-4-acetic acid (12 g.) in cold concentrated sulphuric acid (100 c.c.) was poured on ice (200 g.), stirred mechanically, and powdered sodium dichromate (6 g.) added gradually during 1 hour. Next day, the

green solution was filtered, and almost neutralised with sodium hydroxide solution, and the yellow preciptate produced was washed with water and dried. *4′-Nitro-3-phenyl-2′ : 4-dimethylphthalaz-1-one* crystallised from ethyl acetate in pale yellow needles, m. p. 209—210° (yield, 7 g.; 67·4%) (Found: C, 65·0; H, 4·6; N, 14·5. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·4; N, 14·2%), soluble in alcohol, glacial acetic acid and pyridine. It was insoluble in sodium carbonate solution, but dissolved in sodium hydroxide solution with an orange-red colour; and with mineral acids it formed salts (hydrochloride, colourless needles). With an alcoholic solution of picric acid, it formed a *picrate*, pale yellow needles, m. p. 229—230° (Found: C, 50·4; H, 3·1. $C_{22}H_{16}O_{10}N_6$ requires C, 50·4; H, 3·05%).

Action of methyl sulphate. A solution of 4′-nitro-3-phenyl-2′ : 4-dimethylphthalaz-1-one (1·5 g.) in hot dry nitrobenzene (25 c.c.) was treated with methyl sulphate (0·85 g.) at 95° for 10 minutes. The aqueous residue was filtered from resinous matter and the pale greenish-yellow filtrate gave, when rendered alkaline with sodium carbonate, an orange-red basic product. Crystallisation from ethyl acetate gave *4′-nitro-1-methoxy-3-phenyl-2′-methyl-4-methylene-3 : 4-dihydrophthalazine* (VI) in red prisms, m. p. 118° (yield, 0·9 g.; 57·3%) (Found: C, 66·3; H, 5·0; OMe, 9·8, 9·9. $C_{17}H_{15}O_3N_3$ requires C, 66·0; H, 4·85; OMe, 10·0%). It was readily soluble in mineral acids, forming colourless solutions from which it was reprecipitated on neutralisation.

4′-Amino-3-phenyl-2′ : 4-dimethylphthalaz-1-one.—(a) This was prepared from 1-hydroxy-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine-4-acetic acid (10 g.) and sodium dichromate (3·5 g.). The liquid was filtered, the filtrate almost neutralised with sodium hydroxide, and the yellowish-brown precipitate collected. *4′-Amino-3-phenyl-2′ : 4-dimethylphthalaz-1-one* crystallised from alcohol in pale yellow needles, m. p. 287—288° (yield, 8 g.; 94·5%) (Found: C, 72·4; H, 5·7; N, 15·9. $C_{16}H_{15}ON_3$ requires C, 72·45; H, 5·7; N, 15·85%), soluble in hot water, pyridine, glacial acetic acid and mineral acids (hydrochloride, colourless needles). (b) A solution of 1-hydroxy-3-(4′-amino-2′-methylphenyl)tetrahydrophthalazine-4-acetic acid (5 g.) in water (50 c.c.) and anhydrous sodium carbonate (10 g.) was heated under reflux at about 95° for 10 hours; the product separated progressively in pale yellow needles (yield 2 g.; 47·2%). Better results were obtained by using sodium hydroxide (5 g.) in place of sodium carbonate and filtering off the product at intervals (yield 3 g.; 70·9%), or preferably a solution of potassium hydroxide (3 g.) in alcohol (55 c.c.) and refluxing for 4 hours (yield 4 g.; 94·5%). (c) Reduction of 4′-nitro-3-phenyl-2′ : 4-dimethyl-

phthalaz-1-one with aqueous sodium sulphide. The products in all cases melted at 287—288° and were identical in every respect. The *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 304—305° (Found: C, 70·2; H, 5·7. $C_{18}H_{17}O_2N_3$ requires C, 70·4; H, 5·5%), which on exposure became blue on the surface and then yellow.

1-*Keto*-3-(4′-*amino*-2′-*methylphenyl*)-4-*methyltetrahydrophthalazine*.—A fine suspension of 4′-amino-3-phenyl-2′ : 4-dimethylphthalaz-1-one (4 g.) was reduced similarly to the corresponding unmethylated compound (p. 478). 1-*Keto*-3-(4′-*amino*-2′-*methylphenyl*)-4-*methyltetrahydrophthalazine* crystallised from toluene in pale yellow needles, m. p. 204—205° (yield, 2·5 g.; 62%) (Found: C, 71·8; H, 6·4. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·35%). It was partially reconverted into 4′-amino-3-phenyl-2′ : 4-dimethylphthalaz-1-one when boiled with concentrated hydrochloric acid.

4′-*Amino*-N-*phenyl*-2′ : 3-*dimethylphthalimidine*.—This was prepared from a solution of 4′-amino-3-phenyl-2′ : 4-dimethylphthalaz-1-one (2 g.) in water (50 c.c.), and concentrated hydrochloric acid (50 c.c.) and zinc dust (5 g.). Some *p*-tolylenediamine also was formed. 4′-*Amino*-N-*phenyl*-2′ : 3-*dimethylphthalimidine* crystallised from alcohol in colourless hexagonal prisms, m. p. 183° (yield, 0·8 g.; 42%) (Found: C, 76·1; H, 6·6. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·35%). The *acetyl* derivative crystallised from alcohol in colourless hexagonal prisms, m. p. 231° (Found: C, 73·2; H, 6·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1%).

4′-*Nitro*-3-*phenyl*-2′-*methylphthalaz*-4-*one* (XII).—Alcoholic solutions of equimolecular proportions of *o*-phthalaldehydic acid and 5-nitro-*o*-tolylhydrazine, m. p. 180°, prepared from 5-nitro-*o*-toluidine (compare Davies, J., 1922, **121**, 715), were boiled under reflux (compare J., 1928, 2555). The *lactone* form of o-*carboxybenzaldehyde*-5-*nitro*-o-*tolylhydrazone* (XI) separated in orange-yellow needles, m. p. 225—226° (Found: C, 60·3; H, 4·5. $C_{15}H_{13}O_4N_3$ requires C, 60·2; H, 4·35%), sparingly soluble in dilute hydrochloric acid and soluble in dilute sodium carbonate solution with an orange-red colour. Water was eliminated by dissolving the compound in the minimum quantity of warm concentrated sulphuric acid and next day pouring the solution into water, or preferably by means of amyl-alcoholic hydrogen chloride (compare Aggarwal, Darbari, and Rây, *loc. cit.*). 4′-*Nitro*-3-*phenyl*-2′-*methylphthalaz*-4-*one* crystallised from alcohol in colourless needles, m. p. 187—188° (Found: C, 64·3; H, 4·0. $C_{15}H_{11}O_3N_3$ requires C, 64·1; H, 3·9%). It was insoluble in alkalis, did not form salts with mineral acids, did not form a picrate, and did not react with methyl sulphate.

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us (F. J. S.) to take part in this work, to Dr. A. T. Peters for his assistance with the preparation and analysis of some of the compounds described, and to J. W. Leitch & Co. for gifts of 5-nitro-*o*-toluidine.

CLOTHWORKERS' RESEARCH LABORATORY,
LEEDS UNIVERSITY. [*Received, December 23rd*, 1931.]