162. *A Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part XXI. Derivatives of 2′ : 4′-Dinitrobenzene-2-naphthol-1-diazosulphonate.*

By (the late) F. M. Rowe and W. Osborn.

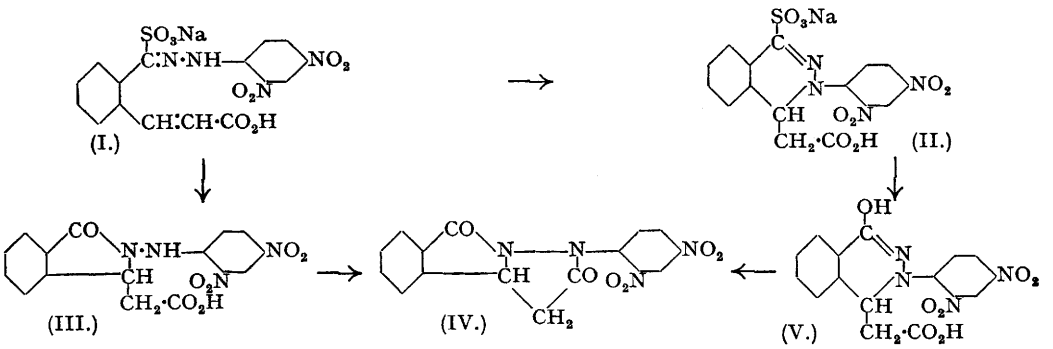
As a result of the presence of the two nitro-groups, sodium 1-(2′ : 4′-dinitrobenzeneazo)-β-naphthaquinone-1-sulphonate is readily converted into *sodium benzaldehyde* 2′ : 4′-*dinitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid* (I), which is the most stable compound of this type yet examined (cf. Rowe, McFadyen, and Peters, this vol., p. 468). With aqueous sulphuric acid (b. p. 140°), 1-*hydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid* (V) behaves abnormally, giving 2-(2′ : 4′-*dinitrophenylamino*)*iso*indolinone-3-*acetic acid* (III) and 1 : 4-*dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII); the latter is convertible by sulphuric acid at 180° into 2′ : 4′-*dinitro*-3-*phenylphthalaz*-4-*one*. Other anomalies of this series of compounds are described and, where possible, derivatives of the 2′ : 4′-dinitro-series are correlated with analogues of the 2′- and 4′-nitro-series.

The naphthalene ring in certain sodium 1-arylazo-β-naphthaquinone-1-sulphonates undergoes fission on addition of sodium hydroxide, with formation of sodium benzaldehyde arylhydrazone-ω-sulphonate-2-β-acrylic acids (Rowe *et al.*, *J.*, 1935, 1796; 1936, 1098). Under suitable conditions ring closure of these open-chain compounds can then be effected to yield either a 2-(nitroarylamino)*iso*indolinone-3-acetic acid, *via* a benzo-nitroarylhydrazide-2-β-acrylic acid, or a sodium hydrogen 3-(nitroaryl)-3 : 4-dihydrophthalazine-1-sulphonate-4-acetate. This possibility of ring closure in one of two directions according to the conditions was originally thought to be limited to compounds containing a nitro-group in the 2′-position, but it has recently been shown that it can also be effected with compounds containing a nitro-group in the 4′-position (Rowe and Cross, *J.*, this vol., p. 461; Rowe, McFadyen, and Peters, *loc. cit.*). It appeared desirable therefore to examine the series of compounds derived from a sodium 1-arylazo-β-naphthaquinone-1-sulphonate containing nitro-groups in both the 2′- and the 4′-position to obtain further evidence with regard to the constitutions of the compounds and their inter-relationships.

Conversion of 2′ : 4′-dinitrobenzene-2-naphthol-1-diazosulphonate through sodium 1-(2′ : 4′-dinitrobenzeneazo)-β-naphthaquinone-1-sulphonate into *sodium benzaldehyde* 2′ : 4′-*dinitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid* (I) proceeds readily, but much more 2′ : 4′-dinitrobenzeneazo-β-naphthol is formed than in analogous cases even at 0°, whilst above 10° complete conversion into 2′ : 4′-dinitrobenzeneazo-β-naphthol occurs.

A notable effect of the additional nitro-group is the remarkable stability of compound (I).

Whereas analogous sodium benzaldehyde nitroarylhydrazone-ω-sulphonate-2-β-acrylic acids are very rapidly converted by aqueous sodium hydroxide into the corresponding sodium hydrogen 3-(nitroaryl)-3 : 4-dihydrophthalazine-1-sulphonate-4-acetates, the most stable yet examined, *viz.*, the compound derived from 2 : 6-dichloro-4-nitroaniline (Rowe, McFadyen, and Peters, *loc. cit.*), being entirely converted within 3 hours from the addition to the sodium hydroxide, no *sodium hydrogen* 3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-

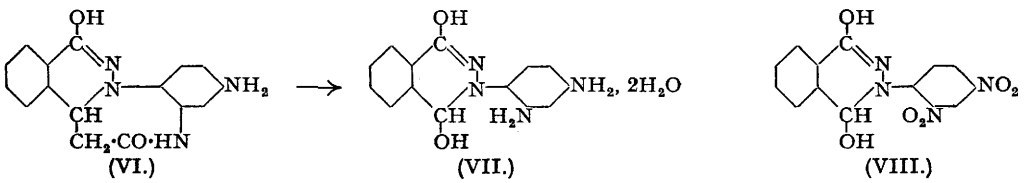


acetate (II) can be detected under 45 minutes from the addition of the sodium hydroxide, and traces of (I) are still present even after reaction with sodium hydroxide for 2 days. Moreover, boiling (I) with dilute hydrochloric acid for at least 12 hours is necessary for complete conversion into 2-(2′ : 4′-*dinitrophenylamino*)iso*indolinone*-3-*acetic acid* (III), and none of the intermediate benzo-2′ : 4′-dinitrophenylhydrazide-2-β-acrylic acid can be detected. Compound (III) could neither be nitrosated nor methylated, but the methylated compound, *methyl* 2-(2′ : 4′-*dinitrophenylmethylamino*)iso*indolinone*-3-*acetate*, was synthesised by condensing *o*-carboxycinnamonitrile *via* the acid chloride (*J.*, 1936, 1101) with 1-(2′ : 4′-dinitrophenyl)-1-methylhydrazine to form *benzo*-1′-(2″ : 4″-*dinitrophenyl*)-1′-*methylhydrazide*-2-β-*acrylonitrile*, followed by ring-closure and hydrolysis with methyl-alcoholic hydrogen chloride.

Water is eliminated from (III) with formation of 2 : 5-*diketo*-3-(2′ : 4′-*dinitrophenyl*)iso*indolinopyrazolidocoline* (IV) which is readily reconverted into (III) by diluting a solution in sulphuric acid. Concentrated or aqueous mineral acids have no action on (III) or (IV) except to open the pyrazole ring of the latter. Compound (IV) can also be obtained by nitrating the corresponding 2′- or 4′-nitrophenyl compounds, but (III) cannot be obtained by nitrating 2-(2′- or 4′-nitrophenylamino)*iso*indolinone-3-acetic acid.

Compound (IV) is reduced by iron and acetic acid to 2 : 5-*diketo*-3-(2′-*nitro*-4′-*aminophenyl*)-iso*indolinopyrazolidocoline* which could not be reduced further, nor could the pyrazole ring be opened by hydrolysis.

Compound (I) is completely converted into (II) by the action of aqueous sodium hydroxide at 0° for 6 days. Compound (II) is also more resistant to hydrolysis than are analogous compounds, and prolonged boiling with dilute hydrochloric acid is necessary for complete conversion into 1-*hydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid* (V). When (V) is refluxed with acetic anhydride and pyridine, (IV) is obtained eventually, although in not quite as good a yield as when (III) is similarly treated.



Compound (V) is reduced by stannous chloride and hydrochloric acid to 1-*hydroxy*-3-(2′ : 4′-*diaminophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid lactam* (VI), but the corresponding acid could not be obtained. When (VI) was refluxed with sulphuric acid (b. p. 140°), 1 : 4-*dihydroxy*-3-(2′ : 4′-*diaminophenyl*)-3 : 4-*dihydrophthalazine dihydrate* (VII) was formed. Attempts to remove the elements of water from the latter caused degradation of the compound, which could not be obtained by reduction of the corresponding dinitro-derivative (VIII).

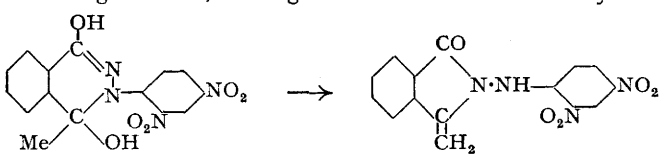
The action of mineral acids under various conditions on (V) was of considerable interest.

Refluxing (V) with sulphuric acid (b. p. 140°) gave a mixture of 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid (III) and 1 : 4-*dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII), this unusual result being clearly due to the presence of the two nitro-groups. 2-(2′ : 4′-Dinitrophenylamino)*iso*indolinone-3-acetic acid (III) was obtained whenever 1-hydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (V) was treated with reagents which tend to attack the 3-nitrogen atom, *i.e.*, in all acid reactions or oxidations, and its formation involves an intermediate open-chain derivative, which is unstable and convertible into (III) under the conditions used.

The reason for the structure of (VIII) is clear when its reactions are considered. It will not form salts with mineral acids, or a picrate or perchlorate, and it cannot be dehydrated with the usual reagents, whilst concentrated sulphuric acid at 180° causes not only dehydration, but also simultaneous isomerisation to 2′ : 4′-*dinitro*-3-*phenylphthalaz*-4-*one*. Thus, the two nitro-groups in the nitrophenyl nucleus completely inhibit any salt formation on the 3-nitrogen atom. Consequently, dehydration with formation of the 3-arylphthalaz-1-one is impossible with a derivative of 2 : 4-dinitroaniline. A more convenient method of obtaining (III) and (VIII) was to add concentrated sulphuric acid to a boiling acetic acid solution of (V) and pour the solution into water. This method was examined with a number of 1-hydroxy-3-(nitroaryl)-3 : 4-dihydrophthalazine-4-acetic acids; all gave the nitro-3-phenylphthalaz-1-one satisfactorily, whilst 1-hydroxy-3-(4′-chloro-2′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid gave 2-(4′-chloro-2′-nitrophenylamino)*iso*indolinone-3-acetic acid in addition.

With concentrated sulphuric acid at 180° for 2—3 minutes, (V) gave the same compounds in diminished yield, whilst after 20 minutes the products were 2′ : 4′-dinitro-3-phenylphthalaz-4-one with some (III). Heating (V) with fuming hydrochloric acid at 180° gave 2′ : 4′-*dinitro*-3-*phenyl*-1-*methylphthalaz*-4-*one* and a little (III), whilst fuming nitric acid or acid dichromate gave a mixture of 1 : 4-*dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine* (IX) and (III). On the other hand, fuming nitric acid converted 1-hydroxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid into 4′-nitro-3-phenyl-4-methylphthalaz-1-one.

When 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine (VIII) was treated with chromium trioxide in acetic acid solution at 40°, immediate oxidation to *phthalyl*-2′ : 4′-*dinitrophenylhydrazide* occurred, none of the intermediate 1 : 4-*diketo*-3-(2′ : 4′-*dinitrophenyl*) *tetrahydrophthalazine* being detected, although the latter was obtained by oxidation of (V) with

(IX.)  (X.)

potassium permanganate at 80°, whilst treatment of (V) with potassium permanganate at 60° gave 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid (III). Nitro-3-arylphthalaz-1-ones, however, were unaffected by chromium trioxide under similar conditions.

Heating (VIII) with dilute hydrochloric acid at 190° (*J.*, 1937, 90) gave 2′ : 4′-dinitro-3-phenylphthalaz-4-one together with an intermediate open-chain compound.

2′ : 4′-Dinitro-3-phenylphthalaz-4-one was synthesised from *o*-phthalaldehydic acid and 2 : 4-dinitrophenylhydrazine *via* o-*carboxybenzaldehyde* 2′ : 4′-*dinitrophenylhydrazone* (cf. *J.*, 1936, 312), but attempts to prepare it by nitrating 4′- or 2′-nitro-3-phenylphthalaz-4-one were unsuccessful.

1 : 4-Dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine (IX) could not be methylated with methyl sulphate, but, when it was crystallised from methyl alcohol containing a trace of mineral acid, 1-*hydroxy*-4-*methoxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine* was formed, which was reconverted into (IX) by boiling ammonia. 1 : 4-Dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine (VIII), however, was readily methylated with methyl sulphate, and the primary product combines with alcohols to form ethers typical of the nitro-3-arylphthalaz-1-ones.

1 : 4-Dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine (IX) was readily oxidised with chromium trioxide to phthalyl-2′ : 4′-dinitrophenylhydrazide, whereas 2′-, 3′-, or 4′-nitro-3-aryl-4-methylphthalaz-1-ones were unaltered. Treatment of (IX) with concentrated sulphuric acid at 180° caused dehydration and isomerisation to 2′ : 4′-dinitro-3-phenyl-1-methylphthalaz-4-one, whilst the action of dilute hydrochloric acid at 190° gave 2-(2′ : 4′-*dinitrophenylamino*)-3-*methylene*iso*indolinone* (X), which was readily converted into 2′ : 4′-dinitro-3-phenyl-1-methylphthalaz-1-one by heating with concentrated sulphuric acid at 180°.

Oxidation of (X) with chromium trioxide gave phthalyl-2′ : 4′-dinitrophenylhydrazide, whilst boiling alcoholic sodium ethoxide opened the ring with formation of o-*carboxyacetophenone*-2′ : 4′-*dinitrophenylhydrazide*, the latter being most readily prepared, however, by condensing acetophenone-*o*-carboxylic acid with 2 : 4-dinitrophenylhydrazine. The only method by which this hydrazide could be converted into 2′ : 4′-dinitro-3-phenyl-1-methylphthalaz-4-one was by heating with concentrated sulphuric acid at 180°.

In an attempt to synthesise 1 : 4-diketo-3-(2′ : 4′-dinitrophenyl)tetrahydrophthalazine (cf. Rowe, Gillan, and Peters, *J.*, 1935, 1811), phthalic anhydride was condensed with 2 : 4-dinitrophenylhydrazine in cold chloroform to form o-*carboxybenzo*-2′ : 4′-*dinitrophenylhydrazide*, which was converted by boiling with acetic acid into phthalyl-2′ : 4′-dinitrophenylhydrazide, but refluxing the latter with alcoholic sodium hydroxide merely gave *o*-carboxybenzo-2′ : 4′-dinitrophenylhydrazide.

Experimental.

Fuller details of preparation are given for the corresponding analogues (*J.*, 1926, 699; 1935, 1800; 1936, 1102).

Sodium Benzaldehyde 2′ : 4′-Dinitrophenylhydrazone-ω-sulphonate-2-β-acrylic Acid (I).—A filtered solution of commercial 50% sodium-β-naphthol-1-sulphonate (48 g.) in water (150 c.c.) was stirred rapidly at 0° into a solution of diazotised 2 : 4-dinitroaniline, prepared by stirring the base (18·3 g.) with a mixture of sodium nitrite (10 g.) and concentrated sulphuric acid (60 c.c.), leaving the resultant paste for 2 hours to form a clear brown solution, and then pouring it on ice (200 g.). 2′ : 4′-Dinitrobenzene-2-naphthol-1-diazosulphonate separated as a purplish-brown paste, which was filtered off, washed free from acid with ice-cold water, pasted with ice-cold water (120 c.c.), and treated with an ice-cold solution of sodium carbonate (30 g.) in water (100 c.c.). Almost colourless plates of sodium 1-(2′ : 4′-dinitrobenzeneazo)-β-naphthaquinone-1-sulphonate began to separate from the pinkish-orange solution after 10 minutes, and the ice-cold suspension was then added to an ice-cold solution of sodium hydroxide (25 g.) in water (100 c.c.). In order to obtain the maximum yield, the thick bordeaux-red paste was acidified after 25 minutes with concentrated hydrochloric acid; it was then made alkaline and filtered from 2′ : 4′-dinitrobenzeneazo-β-naphthol (9 g.; 27·9%). The cold filtrate was faintly acidified with hydrochloric acid; on standing, the sodium hydrogen salt separated as a light sand-coloured precipitate, which crystallised from hot water in small orange-red prisms containing 1 mol. of H_2O (34 g.; 71·5% calc. on the 2 : 4-dinitroaniline) (Found: S, 6·6; H_2O, 3·7. $C_{16}H_{11}O_9N_4SNa,H_2O$ requires S, 6·7; H_2O, 3·8%). It is an orange acid dye, fugitive to light.

2-(2′ : 4′-*Dinitrophenylamino*)iso*indolinone*-3-*acetic Acid* (III).—(*a*) The preceding sodium salt (I) (5 g.) was dissolved in boiling water (200 c.c.), concentrated hydrochloric acid (20 c.c.) added dropwise during 2 hours, and boiling continued until evolution of sulphur dioxide had ceased (12 hours). The reddish-brown precipitate was solely (III) (2·4 g.; 61·4%), no trace of the intermediate benzo-2′ : 4′-dinitrophenylhydrazide-2-β-acrylic acid being detected. (*b*) The best method was to dissolve 2 : 5-diketo-3-(2′ : 4′-dinitrophenyl)*iso*indolinopyrazolidocoline (IV) (5 g.) in concentrated sulphuric acid (25 c.c.) and pour it on ice (100 g.) (5 g.; 95·2%). (*c*) It was also obtained as a by-product in the preparation of 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine and its 4-methyl derivative from 1-hydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (see p. 834). The *acid* crystallised from acetic acid or alcohol in light yellow needles, m. p. 270° (Found: C, 51·7; H, 3·6; N, 15·1. $C_{16}H_{12}O_7N_4$ requires C, 51·6; H, 3·3; N, 15·05%). It dissolves in sodium carbonate and sodium hydroxide solutions with yellowish-brown and deep crimson colours, respectively. It is unaltered by refluxing with aqueous sulphuric acid (b. p. 140°), but refluxing with alcoholic sulphuric or hydrochloric acid gives the ester. The *methyl* ester crystallised from methyl alcohol in light yellow plates, m. p. 183° (Found: C, 52·5; H, 4·0; N, 14·55. $C_{17}H_{14}O_7N_4$ requires C, 52·8; H, 3·65; N, 14·5%). The *ethyl* ester crystallised from ethyl alcohol in light yellow plates, m. p. 153° (Found: C, 53·9; H, 4·3; N, 14·3. $C_{18}H_{16}O_7N_4$ requires C, 54·0; H, 4·0; N, 14·0%). The *anilide* crystallised from acetic acid in yellow needles, m. p. 274° (Found: N, 15·8. $C_{22}H_{17}O_6N_5$ requires N, 15·65%).

2 : 5-*Diketo*-3-(2′ : 4′-*dinitrophenyl*)iso*indolinopyrazolidocoline* (IV).—(*a*) Compound (III) (30 g.) was refluxed with acetic anhydride (75 c.c.) and pyridine (3 c.c.) for 1 hour; the product crystallised on cooling (21 g.; 73·6%). (*b*) 2 : 5-Diketo-3-(2′-nitrophenyl)*iso*indolinopyrazolidocoline (1 g.) was treated with fuming nitric acid (*d* 1·5; 3 c.c.) at room temperature for 10 minutes, then poured on ice (10 g.) and the precipitate collected (1 g.; 87·6%). (*c*) 2 : 5-Diketo-3-(4′-nitrophenyl)*iso*indolinopyrazolidocoline (1 g.) was nitrated as described under (*b*) above (1·1 g.; 96·4%). (*d*) Compound (V) (10 g.) was refluxed with acetic anhydride (25 c.c.) and pyridine (1 c.c.) for 20 hours; the product crystallised on cooling (5·6 g.; 58·8%). The presence of pyridine was essential for this conversion, compound (V) being recovered unaltered in its absence. 2 : 5-*Diketo*-3-(2′ : 4′-*dinitrophenyl*)iso*indolinopyrazolidocoline* crystallised from acetic acid in light yellow, prismatic needles, m. p. 239° (Found: C, 54·2; H, 2·9; N, 15·6. $C_{16}H_{10}O_6N_4$ requires C, 54·25; H, 2·8; N, 15·8%), insoluble in cold dilute mineral acids or alkalis, but soluble in concentrated sulphuric acid, 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid being precipitated on diluting the solution.

2:5-*Diketo*-3-(2′-*nitro*-4′-*aminophenyl*)iso*indolinopyrazolidocoline*.—Compound (IV) (10 g.) was dissolved in acetic acid (300 c.c.), the solution diluted with water (60 c.c.), and then iron powder (6 g.) added to the boiling solution during 7 minutes. Boiling was continued for a further 3 minutes (charcoal), and the solution filtered hot; crystals separated on cooling. 2 : 5-*Diketo*-3-(2′-*nitro*-4′-*aminophenyl*)iso*indolinopyrazolidocoline* crystallised from aqueous acetic acid in orange, flat prisms, m. p. 276° (Found: C, 59·3; H, 3·85; N, 17·6. $C_{16}H_{12}O_4N_4$ requires C, 59·25; H, 3·7; N, 17·3%). It forms with concentrated mineral acids colourless, water-soluble salts, and the solutions readily diazotise and couple with β-naphthol to form a red dye. It neither forms a triazole derivative nor an anhydro-derivative by the

action of acids or phosphorus pentachloride. The *monoacetyl* compound crystallised from acetic anhydride in almost colourless prisms, m. p. 255° (Found: C, 58·9; H, 4·0; N, 15·0. $C_{18}H_{14}O_5N_4$ requires C, 59·0; H, 3·8; N, 15·3%). The nitro-group in 2 : 5-diketo-3-(2′-nitro-4′-aminophenyl)*iso*indolinopyrazolidocoline or its acetyl derivative could not be reduced satisfactorily, and the former could not be converted into 2-(2′-nitro-4′-aminophenylamino)*iso*indolinone-3-acetic acid by analogous means to those used with (IV).

Benzo-1′-(2″ : 4″-dinitrophenyl)-1′-methylhydrazide-2-β-acrylonitrile.—*o*-Carboxycinnamonitrile (0·5 g.) and phosphorus pentachloride (0·5 g.) were heated to 110° for 30 minutes; the phosphorus oxychloride was then distilled off under reduced pressure at 100°, and the solid residue of acid chloride dissolved in cold chloroform (10 c.c.) and filtered into a solution of 1-(2′ : 4′-dinitrophenyl)-1-methylhydrazine (0·7 g.) in chloroform (50 c.c.). The resultant orange suspension was boiled for 10 minutes, water (50 c.c.) and hydrochloric acid (1·5 c.c.) were added, and chloroform was distilled off and the precipitate collected. The *nitrile* crystallised from methyl alcohol in long, colourless, flat prisms, m. p. 189° (1 g.; 94·3%) (Found: C, 55·8; H, 3·65; N, 19·1. $C_{17}H_{13}O_5N_5$ requires C, 55·6; H, 3·6; N, 19·1%).

Methyl 2-(2′ : 4′-*Dinitrophenylmethylamino*)*iso*indolinone-3-*acetate*.—The above nitrile (0·5 g.) was suspended in dry methyl alcohol (20 c.c.) and saturated with dry hydrogen chloride at 0°. Next day, the mixture was refluxed for 1 hour, evaporated to 10 c.c., and crystallised. The *ester* crystallised from methyl alcohol in long, pale yellow needles, m. p. 197° (0·4 g.; 73·4%) (Found: C, 54·0; H, 4·2; N, 14·1. $C_{18}H_{16}O_7N_4$ requires C, 54·0; H, 4·0; N, 14·0%), insoluble in cold aqueous alkalis or mineral acids.

Sodium Hydrogen 3-(2′ : 4′-*Dinitrophenyl*)-3 : 4-*dihydrophthalazine-1-sulphonate-4-acetate* (II).—(*a*) A solution of sodium 1-(2′ : 4′-dinitrobenzeneazo)-β-naphthaquinone-1-sulphonate in sodium hydroxide, prepared as described under (I) (p. 832), instead of being acidified after 25 minutes, was kept ice-cold for 6 days and then acidified. After removal of 2′ : 4′-dinitrobenzeneazo-β-naphthol (8·4 g.; 26%), the sodium hydrogen *salt* was isolated in the usual manner. It crystallised from hot water in bright yellow prisms, m. p. 230° (decomp.) (38 g.; 71·7%) (Found: S, 5·9; H_2O, 12·9. $C_{16}H_{11}O_9N_4SNa,4H_2O$ requires S, 6·0; H_2O, 13·6%). It is a yellow acid dye fugitive to light.

(*b*) Sodium benzaldehyde 2′ : 4′-dinitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid (4 g.), dissolved in sodium hydroxide (6 g.) and water (100 c.c.), was kept ice-cold for 6 days, then acidified with hydrochloric acid; yellow needles crystallised (3·6 g.; 90%). If the sodium hydroxide solution was kept at room temperature, the product was a black tar (2 g.) which, however, was convertible into 1-hydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid by hydrolysis.

Action of Sodium Hydroxide on Sodium 1-(2′ : 4′-*Dinitrobenzeneazo*)-β-*naphthaquinone*-1-*sulphonate*.—Sodium 1-(2′ : 4′-dinitrobenzeneazo)-β-naphthaquinone-1-sulphonate (212 g. in 2700 c.c. of water containing 150 g. of sodium carbonate), prepared as above, was poured into an aqueous solution (500 c.c.) of sodium hydroxide (125 g.) and measured quantities (200 c.c.) removed after various intervals of time. The aliquots were immediately acidified, boiled, and filtered from 2′ : 4′-dinitrobenzeneazo-β-naphthol, and the resulting solution of the sodium sulphonates was hydrolysed by boiling 10% hydrochloric acid into a mixture of (III) and (V), the percentage of (III) being determined from the amount of (IV) formed by refluxing with acetic anhydride and pyridine for 1 minute. The percentages of the compounds isolated are tabulated below.

Time of reaction with sodium hydroxide.	2′ : 4′-Dinitrobenzeneazo-β-naphthol.	2-(2′ : 4′-Dinitrophenylamino)*iso*indolinone-3-acetic acid.	1-Hydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid.
17 seconds	49·8	30·2	—
5 minutes	44·6	35·4	—
15 minutes	40·7	39·3	—
30 minutes	37·2	42·8	—
1 hour	35·6	42·2	2·2
2 hours	30·9	43·4	5·7
4 hours	31·1	39·5	9·4
6 hours	31·3	35·2	13·5
8 hours	31·0	31·9	17·1
24 hours	31·4	15·4	33·2
48 hours	31·0	3·3	45·7

1-*Hydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid*. (V).—A solution of (II) (5 g.) in water (200 c.c.) was boiled, and concentrated hydrochloric acid (20 c.c.) added during 2 hours. Boiling was continued until evolution of sulphur dioxide had ceased (10—12 hours) and the product had separated as an orange-brown precipitate. The *acid* crystallised from ethyl acetate in orange-yellow needles, m. p. 236° (2·9 g.; 83·1%) (Found: C, 51·4; H, 3·2; N, 15·2. $C_{16}H_{12}O_7N_4$ requires C, 51·6; H, 3·3; N, 15·05%). It dissolves in aqueous sodium carbonate and hydroxide with yellowish-brown and deep crimson colours, respectively. Refluxing with acetic anhydride and pyridine for 20 hours gives 2 : 5-diketo-3-(2′ : 4′-dinitrophenyl)*iso*indolinopyrazolidocoline (IV). The *methyl* ester, prepared by the methyl alcohol–hydrogen chloride method, crystallised from methyl alcohol in pale yellow leaflets, m. p. 154° (Found: C, 53·0; H, 3·65; N, 14·4. $C_{17}H_{14}O_7N_4$ requires C, 52·8; H, 3·65; N, 14·5%). The *ethyl* ester crystallised from ethyl alcohol in light yellow plates, m. p. 150° (Found: C, 54·1; H, 4·1; N, 13·8. $C_{18}H_{16}O_7N_4$ requires C, 54·0; H, 4·0; N, 14·0%). The *anilide* crystallised from glacial acetic acid in yellow prismatic needles, m. p. 277° (Found: N, 15·55. $C_{22}H_{17}O_6N_5$ requires N, 15·65%).

1-*Keto*-3-(2′ : 4′-*dinitrophenyl*)-2-*methyltetrahydrophthalazine*-4-*acetic Acid*.—(*a*) Compound (V) (2 g.) was dissolved in water (4 c.c.), methyl alcohol (24 c.c.), and potassium hydroxide (4 g.), and methyl sulphate (3 c.c.) was added to the boiling deep purple solution during 15 minutes. After refluxing for a further 15 minutes, the solution was cooled and just acidified with hydrochloric acid, and the precipitate collected and macerated with sodium carbonate. Acidification of the extract gave 1-keto-3-(2′ : 4′-di-

nitrophenyl)-2-methyltetrahydrophthalazine-4-acetic acid (0·2 g.; 9·6%), whilst the insoluble residue was the methyl ester (1·5 g.; 69·6%). (*b*) Methyl 1-keto-3-(2′ : 4′-dinitrophenyl)-2-methyltetrahydrophthalazine-4-acetate was hydrolysed by warm sodium carbonate for 5 minutes. 1-*Keto*-3-(2′ : 4′-*dinitrophenyl*)-2-*methyltetrahydrophthalazine*-4-*acetic acid* crystallised from methyl alcohol in light yellow prisms, m. p. 278° (Found: C, 53·1; H, 3·9; N, 14·3. $C_{17}H_{14}O_7N_4$ requires C, 52·8; H, 3·6; N, 14·4%). The *methyl* ester, prepared as described under (*a*) above, was also obtained by methylating 1-keto-3-(2′ : 4′-dinitrophenyl)-2-methyltetrahydrophthalazine-4-acetic acid, or by dissolving methyl 1-keto-3-(2′-nitrophenyl)-2-methyltetrahydrophthalazine-4-acetate (1 g.) in fuming nitric acid (*d* 1·5; 5 c.c.) at room temperature and pouring on ice (25 g.) after 5 minutes (1·1 g.; 97·5%). It crystallised from methyl alcohol in orange-yellow prisms, m. p. 167° (Found: C, 54·0; H, 4·1; N, 14·3. $C_{18}H_{16}O_7N_4$ requires C, 54·0; H, 4·0; N, 14·0%).

1-*Hydroxy*-3-(2′ : 4′-*diaminophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid Lactam* (VI).—Compound (V) (20 g.) was added quickly to a boiling solution of stannous chloride (100 g.) in concentrated hydrochloric acid (250 c.c.). After the vigorous reaction had ceased, boiling was continued for 10 minutes, concentrated hydrochloric acid (250 c.c.) added, and the solution left to crystallise. The brownish-yellow crystals were dissolved in water, tin was removed by hydrogen sulphide, the filtrate boiled, and the hydrochloride of the lactam filtered off. It was basified with boiling, very dilute alkali, and the resultant yellow needles were washed with water, alcohol, and ether. The *lactam*, yellow needles, m. p. 290° (6·5 g.; 41·1%) (Found: C, 65·1; H, 4·7; N, 18·8. $C_{16}H_{14}O_2N_4$ requires C, 65·3; H, 4·8; N, 19·0%), is insoluble in water, organic solvents, and aqueous alkalis, but with concentrated mineral acids forms colourless water-soluble salts which diazotise readily and couple with β-naphthol to form a red dye. The *monoacetyl* derivative, obtained with acetic anhydride and a little pyridine, crystallised from aqueous alcohol in colourless plates, m. p. 306° (Found: C, 64·15; H, 4·8; N, 16·7. $C_{18}H_{16}O_3N_4$ requires C, 64·3; H, 4·8; N, 16·7%).

Action of Nitric Acid on 1-*Hydroxy*-3-(2′-*aminophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid Lactam*.—The lactam (1 g.) was added during 1 minute to fuming nitric acid (*d* 1·5; 10 c.c.) at room temperature, and after 5 minutes the mixture was poured on ice (50 g.) and left to crystallise. On warming the yellow crystals with aqueous ammonia and crystallising from aqueous acetic acid, almost colourless prisms of 2′-amino-3-phenylphthalaz-1-one-4-acetic acid lactam, m. p. 298° (*J.*, 1935, 1807), were obtained. A similar experiment with 1-hydroxy-3-(2′ : 4′-diaminophenyl)-3 : 4-dihydrophthalazine-4-acetic acid lactam was unsuccessful.

1 : 4-*Dihydroxy*-3-(2′ : 4′-*diaminophenyl*)-3 : 4-*dihydrophthalazine Dihydrate* (VII).—Compound (VI) (2 g.) was macerated with concentrated sulphuric acid (20 c.c.) and the white paste was dissolved in water (24 c.c.). The clear red solution was refluxed for 2 hours, cooled, poured on ice (100 g.), and nearly neutralised with sodium carbonate. The pale yellow solid, which separated, crystallised from methyl alcohol in yellow, prismatic needles, m. p. 151° (1·3 g.; 62·4%) (Found: C, 55·0; H, 5·6; N, 18·5. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%). It is slightly soluble in cold water with an orange colour, deepened by the addition of alkali, soluble in dilute mineral acids, and diazotises and couples with β-naphthol to form a red dye. Attempted reduction to *p*-amino-*o*-benzylenebenziminazole was unsuccessful.

1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII).—(*a*) Compound (V) (5 g.) was macerated with concentrated sulphuric acid (50 c.c.) and water (60 c.c.), the fine suspension refluxed for 6 hours (a solution was obtained after 2 hours), cooled, and poured on ice (200 g.), and the yellow precipitate ground with aqueous sodium carbonate. Acidification of the extract and crystallisation of the precipitate from acetic acid gave light yellow needles of 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid, m. p. and mixed m. p. 270° (4 g.; 80%). The sodium carbonate-insoluble residue was 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine (0·3 g.; 6·8%).

(*b*) Compound (V) (5 g.) was dissolved in boiling acetic acid (50 c.c.), and concentrated sulphuric acid (25 c.c.) was added. Boiling was continued for 10 minutes, the solution then poured into water (400 c.c.) and the precipitate rapidly filtered off; the filtrate slowly deposited brownish-yellow crystals. The two precipitates were combined and extracted with aqueous sodium carbonate. The alkali-soluble portion was 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid (2·9 g.; 58%) and the alkali-insoluble compound was 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine (1·45 g.; 34·5%). The percentage yields of the two compounds isolated under various conditions are tabulated below.

Wt. of (V) (g.).	Vol. of acetic acid (c.c.).	Vol. of sulphuric acid (c.c.).	Final temp. of solution.	Vol. of water (c.c.).	*a* (%).	*b* (%).
2	20	2	128°	150	98·5	—
2	20	6	131	250	75·0	22·5
2	20	10	138	250	58·0	34·5
2	20	16	165	250	50·2	29·3
2	20	20	175	300	50·5	29·0
2	20	40	185	350	50·5	29·0
2	2	20	200	300	15·0	19·5

a, 2-(2′ : 4′-Dinitrophenylamino)*iso*indolinone-3-acetic acid.
b, 1 : 4-Dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine.

(*c*) Compound (V) (2 g.) was heated with concentrated sulphuric acid (20 c.c.) at 180° for 3 minutes, and the solution was cooled and poured on ice (50 g.). The precipitate was a mixture of 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid (0·47 g.; 23·5%) and 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine (0·4 g.; 28·2%). Longer heating (15—20 minutes) with sulphuric acid converted the 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine into 2′ : 4′-dinitro-3-phenylphthalaz-4-one (see p. 835).

1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* crystallised from methyl alcohol or benzene–pyridine in light yellow prisms, m. p. 223° (Found : C, 50·8; H, 3·2; N, 17·0. $C_{14}H_{10}O_6N_4$ requires C, 50·9; H, 3·0; N, 17·0%). Attempts to dehydrate the compound with phosphorus trichloride in toluene, acetic anhydride, and pyridine, or cold concentrated sulphuric, acid failed, whilst concentrated sulphuric acid at 180° caused isomerisation to 2′ : 4′-dinitro-3-phenylphthalaz-4-one to occur simultaneously with dehydration (see below).

Nitro-3-arylphthalaz-1-ones. The reaction described under (*b*) above was attempted with other 1-hydroxy-3-(nitroaryl)-3 : 4-dihydrophthalazine-4-acetic acids, the general procedure being to add concentrated sulphuric acid (25 c.c.) to a boiling solution of the nitro-acid (5 g.) in glacial acetic acid (50 c.c.), to continue boiling for 10 minutes, and then to pour the solution into water (400 c.c.). Where necessary, the solution was partly neutralised with sodium carbonate. The precipitate was collected and treated as usual.

R = 4′-*Nitrophenyl.* The product was a mixture of the unchanged compound (1 g.; 20%) and 4′-nitro-3-phenylphthalaz-1-one, m. p. and mixed m. p. 333° (3 g.; 73·5%).

R = 2′-*Bromo*-4′-*nitrophenyl.* The product was a mixture of the unchanged compound (1 g.; 20%) and 2′-bromo-4′-nitro-3-phenylphthalaz-1-one, which crystallised from ethyl acetate in light brown plates, m. p. 209° (not 197° as previously described; *J.*, 1935, 1136) (2·1 g.; 49·3%). Attempts to methylate this compound were unsuccessful.

R = 2′-*Chloro*-4′-*nitrophenyl.* The product was a mixture of the unchanged compound (0·8 g.; 16·1%) and 2′-chloro-4′-nitro-3-phenylphthalaz-1-one, which crystallised from alcohol in yellow needles, m. p. 196° (not 130—150° as previously described; *J.*, 1932, 17) (1·95 g.; 46·7%). Attempts to methylate this compound were unsuccessful.

R = 4′-*Chloro*-2′-*nitrophenyl.* The immediate precipitate on pouring the solution into water was the unchanged compound (1·05 g.; 21%), whilst the subsequent crystalline precipitate was a mixture of 2-(4′-chloro-2′-nitrophenylamino)*iso*indolinone-3-acetic acid, m. p. and mixed m. p. 278° (0·3 g.; 6%), and 4′-chloro-2′-nitro-3-phenylphthalaz-1-one, which crystallised from methyl alcohol in long, yellow, prismatic needles, m. p. 263° (not 233° as previously described; *J.*, 1935, 1806) (2 g.; 47·9%) (Found : C, 55·8; H, 2·8; N, 14·0; Cl, 11·4. Calc. for $C_{14}H_8O_5N_3Cl$: C, 55·7; H, 2·65; N, 13·9; Cl, 11·7%). The *picrate* crystallised from methyl alcohol in pale yellow, prismatic needles, m. p. 230° (Found : C, 45·1; H, 2·4; N, 15·7. $C_{20}H_{11}O_{10}N_6Cl$ requires C, 45·2; H, 2·1; N, 15·8%).

Action of Methyl Sulphate on 1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII).—Compound (VIII) (0·55 g.) dissolved in nitrobenzene (12 c.c.) at 110° was treated with methyl sulphate (1 g.) for 1·5 hours. Nitrobenzene was removed by distillation with steam, and the residue cooled and basified. The yellow powder, m. p. 149—153°, was crystallised from either methyl or ethyl alcohol with formation of the corresponding ether. 1 : 4-*Dimethoxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* crystallised in lustrous yellow plates, m. p. 196° (Found : C, 53·8; H, 3·95; N, 16·0. $C_{16}H_{14}O_6N_4$ requires C, 53·65; H, 3·9; N, 15·7%). 1-*Methoxy*-4-*ethoxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* crystallised in lustrous yellow plates, m. p. 197° (Found : C, 55·0; H, 4·1; N, 15·0. $C_{17}H_{16}O_6N_4$ requires C, 54·85; H, 4·3; N, 15·05%). Heating first at 110° and then at 140° for 2 hours merely gives an intractable resin and no 4-keto-1-methoxy-3-(2′ : 4′-dinitrophenyl)-3 : 4-dihydrophthalazine is formed.

Action of Chromium Trioxide on 1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII).—Compound (VIII) (2 g.), dissolved in acetic acid (100 c.c.) at 40°, was treated with chromium trioxide (1·2 g.) with vigorous stirring. After 10 minutes, the deep green solution was poured on ice (250 g.); the yellow precipitate crystallised from acetic acid in pale yellow needles, m. p. 271°, identical with a specimen of synthetic phthalyl-2′ : 4′-dinitrophenylhydrazide (see p. 837), m. p. and mixed m. p. 271° (1·6 g.; 80·5%). Under identical conditions, nitro-3-arylphthalaz-1-ones (R = 3′- or 4′-nitro-, or 4′-chloro-2′-nitrophenyl) were unaffected, and even at 100° were recovered unchanged.

2′ : 4′-*Dinitro*-3-*phenylphthalaz*-4-*one.*—*o*-Phthalaldehydic acid (1·5 g.) dissolved in boiling alcohol (25 c.c.) was slowly poured into a boiling solution of 2 : 4-dinitrophenylhydrazine (2 g.) in alcohol (300 c.c.). After 5—10 minutes' refluxing, the red, flocculent precipitate of *o-carboxybenzaldehyde*-2′ : 4′-*dinitrophenylhydrazone* was crystallised from alcohol; light red, hair-like needles, m. p. 270° after becoming yellow at about 240° (3·2 g.; 96·1%) (Found : C, 50·6; H, 3·1; N, 16·7. $C_{14}H_{10}O_6N_4$ requires C, 50·9; H, 3·0; N, 17·0%). Ring closure was effected only by heating with concentrated sulphuric acid to 180° for 2—3 minutes and then diluting with ice (95% conversion). 2′ : 4′-*Dinitro*-3-*phenylphthalaz*-4-*one* crystallised from methyl alcohol or benzene in green-tinged prisms, m. p. 238° (Found : C, 54·0; H, 2·6; N, 17·8. $C_{14}H_8O_5N_4$ requires C, 53·85; H, 2·6; N, 17·95%). It does not form salts with mineral acids and does not form a picrate or perchlorate. Attempts to prepare it by nitrating the corresponding 4′- or 2′-nitro-compound with fuming nitric acid (*d* 1·5) alone or mixed with concentrated sulphuric acid at 80° failed, the material remaining unaltered.

Conversion of 1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine* (VIII) *into* 2′ : 4′-*Dinitro*-3-*phenylphthalaz*-4-*one.*—(*a*) Compound (VIII) (4 g.) was heated with concentrated sulphuric acid (20 c.c.) at 180° for 5 minutes, the solution cooled and poured on ice (50 g.), and the colourless precipitate well washed with aqueous sodium carbonate; it crystallised from methyl alcohol in green-tinged prisms, m. p. 238° (1·1 g.; 26·0%).

When (V) was heated similarly with sulphuric acid for 20 minutes, the product was a mixture of 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid (III) (0·94 g.; 23·5%) and 2′ : 4′-dinitro-3-phenylphthalaz-4-one (0·47 g.; 13·4%).

(*b*) (i) Compound (VIII) (0·75 g.) heated with aqueous hydrochloric acid (1 : 17; 18 c.c.) at 155° for 6 hours was unchanged. (ii) Compound (VIII) (0·75 g.) heated with aqueous hydrochloric acid (2 : 16; 18 c.c.) at 190° for 6 hours gave a mixture of red needles and orange-yellow prisms, which were separated by aqueous sodium carbonate in which the former were soluble. The alkali-insoluble compound was 2′ : 4′-dinitro-3-phenylphthalaz-4-one (0·35 g.; 42·9%), but the alkali-soluble compound (0·5 g.) was not analogous to any derivative previously obtained. The latter was precipitated by acid; it crystallised from alcohols in red needles, m. p. 270—286°, but the inconsistent analytical results could not be

interpreted. It was clearly an intermediate stage in the formation of 2′ : 4′-dinitro-3-phenylphthalaz-4-one, however, because it yielded that compound in green-tinged prisms, m. p. 238°, when crystallised from toluene or treated with dehydrating agents.

1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine* (IX).—(*a*) Oxidation of (V) with potassium dichromate in aqueous sulphuric acid always gave a mixture of (III) and 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine (IX) readily separable by extracting the former with aqueous sodium carbonate, the relative proportion of the two formed depending on the dilution of the sulphuric acid. Compound (V) (10 g.) was dissolved in concentrated sulphuric acid (75 c.c.), and the solution diluted with ice (100 g.) and stirred for 3 hours, potassium dichromate (5 g.) being added in portions during the first hour. After a time, the precipitate was filtered off and added to the further precipitate obtained by partial neutralisation of the filtrate. The percentage yields of compounds (III) and (IX) isolated under various conditions are tabulated below.

Wt. of (V) (g.).	Vol. of sulphuric acid (c.c.).	Wt. of ice added (g.).	*a* (%).	*b* (%).
10	75	50	98	—
10	75	100	65	16·2
10	75	150	50	40·5
10	75	200	50 *	38·9

a, 2-(2′ : 4′-Dinitrophenylamino)*iso*indolinone-3-acetic acid.
b, 1 : 4-Dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine.
* In this experiment, the alkali-soluble portion was a mixture of unchanged (V) and (III), separable by fractional crystallisation from ethyl acetate.

(*b*) Compound (V) (2 g.) was dissolved in fuming nitric acid (*d* 1·5; 12·5 c.c.). The reaction was vigorous and, after 10 minutes at room temperature, the solution was poured on ice (50 g.) and the yellow precipitate macerated with aqueous sodium carbonate to extract (III) (0·45 g.; 22·5%) from (IX) (0·65 g.; 35·1%). No nitrate of 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine was obtained (see 4′-nitro-3-phenylphthalaz-4-methyl-1-one nitrate below).

1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine* crystallised from benzene–pyridine or methyl alcohol in orange prisms, m. p. 232° (Found : C, 52·4; H, 3·7; N, 16·1. $C_{15}H_{12}O_6N_4$ requires C, 52·3; H, 3·5; N, 16·3%). Attempts to methylate this compound with methyl sulphate failed, as did also attempts to dehydrate it by means of phosphorus trichloride in toluene, acetic anhydride, and pyridine, or cold concentrated sulphuric acid. The action of hot concentrated sulphuric acid is described below.

When (IX) is crystallised from methyl alcohol containing a trace of mineral acid, however, 1-*hydroxy*-4-*methoxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine*, light orange, prismatic needles, m. p. 185°, is obtained (Found : C, 53·55; H, 4·1; N, 15·6. $C_{16}H_{14}O_6N_4$ requires C, 53·65; H, 3·9; N, 15·7%), reconverted into 1 : 4-dihydroxy-3-(2′ : 4′-dinitrophenyl)-4-methyl-3 : 4-dihydrophthalazine by boiling with ammonia (*d* 0·88) for 5 minutes.

4′-*Nitro*-3-*phenyl*-4-*methylphthalaz*-1-*one Nitrate*.—(*a*) 1-Hydroxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (2 g.) was treated with fuming nitric acid (*d* 1·5; 12·5 c.c.). The reaction was vigorous. After 10 minutes, the mixture was poured on ice (50 g.) and the precipitate macerated with aqueous sodium carbonate. The alkali-soluble portion was unchanged 1-hydroxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (0·3 g.; 15%), whilst the insoluble compound was 4′-nitro-3-phenyl-4-methylphthalaz-1-one nitrate (1·23 g.; 60·0%). (*b*) 4′-Nitro-3-phenyl-4-methylphthalaz-1-one (Rowe, Levin, and Peters, *J.*, 1931, 1070) (1 g.) was treated similarly and the *nitrate* was obtained (1·1 g.; 90·1%). It crystallised from methyl alcohol in brown needles, m. p. 169° (Found : C, 52·3; H, 3·5; N, 16·3. $C_{15}H_{12}O_6N_4$ requires C, 52·3; H, 3·5; N, 16·3%), reconverted into the base by boiling with concentrated ammonia.

Action of Chromium Trioxide on 1 : 4-*Dihydroxy*-3-(2′ : 4′-*dinitrophenyl*)-4-*methyl*-3 : 4-*dihydrophthalazine*.—Compound (IX) (1 g.), dissolved in acetic acid (65 c.c.) at 40°, was treated with chromium trioxide (0·5 g.) with vigorous stirring. After 10 minutes, the green solution was poured on ice (100 g.), and the yellow precipitate filtered off, washed well with aqueous sodium carbonate and crystallised from acetic acid; pale yellow prismatic needles, m. p. 271°, identical with a specimen of synthetic phthalyl-2′ : 4′-dinitrophenylhydrazide (see p. 837), m. p. and mixed m. p. 271° (0·5 g.; 55·1%). Under identical conditions, nitro-3-phenyl-4-methylphthalaz-1-ones (R = 2′-, 3′- or 4′-nitrophenyl) were unaffected, and even at 100° were recovered unchanged.

2′ : 4′-*Dinitro*-3-*phenyl*-1-*methylphthalaz*-4-*one*.—(*a*) Equimolecular proportions of acetophenone-*o*-carboxylic acid (*J.*, 1936, 312; 1928, 2555) and 2 : 4-dinitrophenylhydrazine (2 g.) were condensed. *o*-*Carboxyacetophenone* 2′ : 4′-*dinitrophenylhydrazone* crystallised from methyl alcohol in orange-red needles, m. p. 200° (3·34 g.; 96·1%) (Found : N, 16·3. $C_{15}H_{12}O_6N_4$ requires N, 16·3%). Ring closure was effected only by heating it (1 g.) with concentrated sulphuric acid (10 c.c.) at 180° for 2—3 minutes and then pouring on ice (0·8 g.; 84·5%). (*b*) Compound (V) (4 g.) was heated with fuming hydrochloric acid (*d* 1·19; 8 c.c.) at 180° for 2 hours. The solid was filtered off and ground successively with warm aqueous ammonia and 10% aqueous sodium carbonate. The alkali-soluble portion was (III) (0·1 g.; 2·5%), whilst the alkali-insoluble compound was 2′ : 4′-dinitro-3-phenyl-1-methylphthalaz-4-one (2·3 g.; 65·6%). (*c*) A solution of (IX) (2 g.) in concentrated sulphuric acid (10 c.c.) was heated to 180° for 3 minutes, cooled, and poured on ice (1 g.; 52·7%). (*d*) Compound (X) (0·5 g.) was heated with concentrated sulphuric acid (5 c.c.) at 180—185° for 3 minutes, cooled, and poured on ice (0·4 g.; 80%). 2′ : 4′-*Dinitro*-3-*phenyl*-1-*methylphthalaz*-4-*one* crystallised from benzene in almost colourless needles, m. p. 248° (Found : C, 55·1; H, 2·85; N, 17·1. $C_{15}H_{10}O_5N_4$ requires C, 55·2; H, 3·05; N, 17·2%). It does not form salts with mineral acids, does not form a picrate or perchlorate, and is unaffected by heating with aqueous hydrochloric acid (1 : 8) in a sealed tube. Attempts to prepare it by nitrating the corresponding 4′- or 2′-nitro-compound failed, the material remaining unaltered.

2-(2′ : 4′-*Dinitrophenylamino*)-3-*methylene*iso*indolinone* (X).—Compound (IX) (0·75 g.) was heated with aqueous hydrochloric acid (1 : 8; 18 c.c.) at 190° for 6 hours (no action occurred at 150°), and the product ground with dilute hydrochloric acid and washed well with aqueous sodium carbonate. The iso*indolinone* crystallised from methyl alcohol in pale greenish-yellow needles, m. p. 198° (0·4 g.; 56·3%) (Found: C, 55·3; H, 2·95; N, 17·1. $C_{15}H_{10}O_5N_4$ requires C, 55·2; H, 3·05; N, 17·2%). Heating this compound with sulphuric acid at 180° converted it into 2′ : 4′-dinitro-3-phenyl-1-methylphthalaz-4-one, whilst refluxing it (1 g.) with alcoholic sodium ethoxide (0·2 g. sodium in 25 c.c. of alcohol) for 30 minutes, pouring on ice, and acidifying with hydrochloric acid gave *o*-carboxyacetophenone 2′ : 4′-dinitrophenylhydrazone (0·9 g.; 85·3%), and oxidation of it (1 g.) in acetic acid (30 c.c.) at 40° with chromium trioxide (0·5 g.) and pouring on ice gave phthalyl-2′ : 4′-dinitrophenylhydrazide (0·66 g.; 65·8%).

Action of Potassium Permanganate on 1-*Hydroxy*-3-(2′ : 4′-*dinitrophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid*.—(*a*) Treatment of (V) (10 g.) suspended in water (100 c.c.) at 60° with potassium permanganate (15 g.) added slowly during 90 minutes, followed by dilution with water (500 c.c.), filtering from manganese dioxide, and acidifying with hydrochloric acid gave 2-(2′ : 4′-dinitrophenylamino)*iso*indolinone-3-acetic acid, m. p. and mixed m. p. 270° (4·8 g.; 48%).

(*b*) Treatment of (V) (10 g.) suspended in water (50 c.c.) at 80° with potassium permanganate (15 g.) added all at once, and isolation of the product as described under (*a*) above, gave a brownish precipitate of 1 : 4-*diketo*-3-(2′ : 4′-*dinitrophenyl*)*tetrahydrophthalazine*, which crystallised from acetic acid in brownish-yellow prisms, m. p. 271° (1·5 g.; 17·0%) (Found: C, 51·2; H, 2·9; N, 16·8. $C_{14}H_8O_6N_4$ requires C, 51·2; H, 2·5; N, 17·1%).

o-*Carboxybenzo*-2′ : 4′-*dinitrophenylhydrazide*.—2 : 4-Dinitrophenylhydrazine (2 g.) was condensed with phthalic anhydride (1·5 g.) in chloroform (600 c.c.). The *carboxy-hydrazide* crystallised from chloroform in pale yellow, prismatic needles, m. p. 227°, resolidifying and melting at 270° (3 g.; 87·6%) (Found: C, 48·55; H, 3·05; N, 15·9. $C_{14}H_{10}O_7N_4$ requires C, 48·55; H, 2·9; N, 16·2%.

Phthalyl-2′ : 4′-*dinitrophenylhydrazide*.—(*a*) *o*-Carboxybenzo-2′ : 4′-dinitrophenylhydrazide (2 g.) was refluxed with acetic acid (15 c.c.) for 1 hour (1·7 g.; 89·7%). (*b*) The *hydrazide* was also obtained by the oxidation of (VIII), (IX), or (X) with chromium trioxide in acetic acid. It crystallised from acetic acid in pale yellow prismatic needles, m. p. 271° (Found: C, 51·1; H, 2·4; N, 17·2. $C_{14}H_8O_6N_4$ requires C, 51·2; H, 2·5; N, 17·1%). It dissolved on warming in alcoholic sodium hydroxide with a deep reddish-brown colour, and the solution after being refluxed for 18 hours gave some *o*-carboxybenzo-2′ : 4′-dinitrophenylhydrazide but no 1 : 4-diketo-3-(2′ : 4′-dinitrophenyl)tetrahydrophthalazine.

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals.

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[*Received, September 12th,* 1946.]