232. *A Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part XV. Derivatives of 2′-Nitro-4′-methylbenzene-2-naphthol-1-diazosulphonate and Synthesis of 2-(2′-Nitro-4′-methylphenylamino)isoindolinone-3-acetic Acid.*

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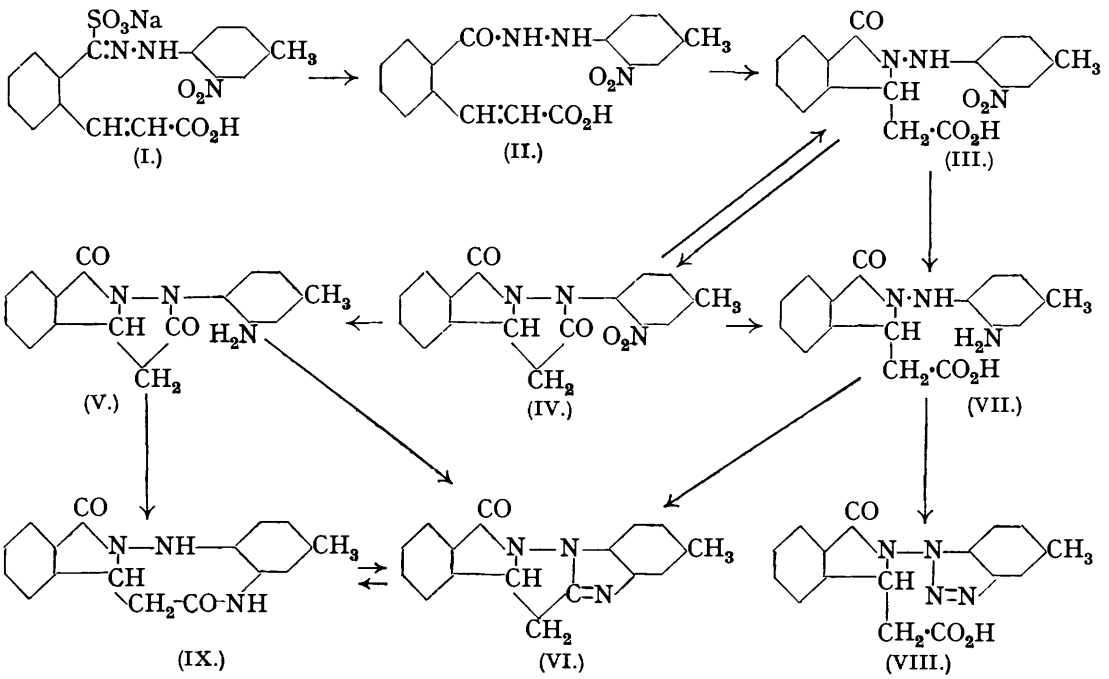
It has been definitely established that the naphthalene ring in certain sodium 1-arylazo-β-naphthaquinone-1-sulphonates undergoes fission on addition of sodium hydroxide, with formation of sodium benzaldehydearylhydrazone-ω-sulphonate-2-β-acrylic acids, by the isolation of the latter in the case of 2′-nitro-substituted compounds and their 4′- and 5′-chloro-derivatives (J., 1935, 1796). Under suitable conditions ring closure of these open-chain compounds can then be effected to yield either a 2-(2′-nitroarylamino)*iso*indolinone-3-acetic acid, ***via*** a benzo-2′-nitroarylhydrazide-2-β-acrylic acid, or a sodium hydrogen 3-(2′-nitroaryl)-3 : 4-dihydrophthalazine-1-sulphonate-4-acetate. Derivatives of both types of compound have been described (*loc. cit.*), but it appeared desirable to obtain further evidence with regard to their constitutions and inter-relationships, particularly in the case of the complex derivatives of 2-(2′-nitroarylamino)*iso*indolinone-3-acetic acids, by examining one further series of 2′-nitro-substituted compounds. Consequently, the investigation

has now been extended to the compounds derived from *m*-nitro-*p*-toluidine, and at the same time the constitution of the 2-(2′-nitroarylamino)*iso*indolinone-3-acetic acids has been confirmed by both degradation and synthesis.

In general, the course of the reactions and the properties of the products in the present series are similar to those observed with the analogous lower homologues containing the nitro- or the amino-group in the 2′-position and with their chloro-derivatives. Nevertheless, in some instances the presence of the 4′-methyl group leads to reactions that could not be effected in the previous series, and in other instances it completely inhibits reactions that were successful in its absence.

Conversion of 2′-nitro-4′-methylbenzene-2-naphthol-1-diazosulphonate through sodium 1-(2′-nitro-4′-methylbenzeneazo)-β-naphthaquinone-1-sulphonate into *sodium benzaldehyde-2′-nitro-4′-methylphenylhydrazone-ω-sulphonate*-2-β-*acrylic acid* (I) proceeds readily and little 2′-nitro-4′-methylbenzeneazo-β-naphthol is formed. Compound (I), which is obtained in excellent yield, is converted by boiling dilute hydrochloric acid into a mixture of *benzo-2′-nitro-4′-methylphenylhydrazide*-2-β-*acrylic acid* (II) and 2-(2′-*nitro*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic acid* (III), the relative proportions depending upon the conditions used. Compound (II) is converted into (III) by boiling with water, dilute sodium carbonate solution, or organic solvents, whilst attempts to prepare derivatives of (II) lead to corresponding derivatives of (III) (cf. the ethylation of *o*-carboxycinnamic acid which gives ethyl phthalideacetate; Roth, *Ber.*, 1914, **47**, 1598).

When 2-(2′-nitro-4′-methylphenylamino)*iso*indolinone-3-acetic acid, or less satisfactorily (II), is refluxed with acetic anhydride and pyridine, or with toluene in presence of phosphorus trichloride, or with thionyl chloride, 1 molecule of water is eliminated, giving 2 : 5-*diketo*-3-(2′-*nitro*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (IV). As a result of this reaction, compound (IV) is also obtained as a by-product in the preparation of the *anilide* of (III). Compound (IV) is reconverted almost quantitatively into (III) when a solution in sulphuric acid is diluted, but further degradation occurs when aqueous-alcoholic sodium hydroxide is used for hydrolysis (see p. 1100).



Reduction of the nitro-compound (IV) with iron and acetic acid yields 2 : 5-*diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (V), which diazotises and couples to

form azo-dyes, and is convertible by boiling acetic anhydride into a mixture of the mono- and the *di-acetyl* derivative, whereas the lower homologue under similar conditions gives the monoacetyl derivative only. Unlike compound (IV), which is readily hydrolysed to (III) by dilute sulphuric acid, when compound (V) is dissolved in dilute sulphuric acid (1 : 1) and heated to the b. p., 1 mol. of water is removed and the sulphate of a new base is obtained; the same base is also formed when (V) is refluxed with toluene in presence of phosphorus trichloride. For the reasons given below, there is no doubt that the base is 2 : 2′-*anhydro*-2 : 5-*diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (VI), which is unaffected by boiling acetic anhydride, does not react with nitrous acid, and forms stable salts with acids. It forms a *picrate*, which is obtained also by the action of alcoholic picric acid on (V) owing to the ease with which water is eliminated from the latter.

Although the limited action of boiling dilute sulphuric acid converts (V) into the 2 : 2′-anhydro-derivative (VI), refluxing (VI) with similarly dilute sulphuric acid for 3 hours results in the addition of 1 molecule of water. The product, however, is not compound (V), but is also obtained similarly from (V), and is the *lactam* (IX) of 2-(2′-*amino*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic acid*. This base forms stable salts with acids and does not react with nitrous acid. It forms a *picrate*, from which it is recovered unaltered by treatment with alkali, in contrast to the behaviour of (V), which yields the picrate of (VI). Compound (IX) is reconverted into compound (VI) by refluxing with toluene in presence of phosphorus trichloride, a reaction which does not occur with the lower homologue or its 4′-chloro-derivative.

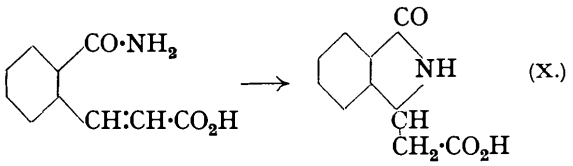
Although it appeared more probable that when 1 molecule of water is removed from compound (V) condensation occurs between the amino-group and the keto-group in position 2 with formation of (VI), hitherto the alternative possibility that the keto-group in position 5 is involved could not be definitely excluded on the basis of the results obtained with the lower homologue and its 4′-chloro-derivative. Consideration of the properties and inter-relationships of the compounds in the present series, however, clearly shows that it is the keto-group in position 2 that is involved in the condensation and that the product is actually compound (VI). Thus, that the link between a carbon atom in position 2 and a nitrogen atom in position 3 is easily hydrolysed by dilute sulphuric acid is shown by the conversion of (IV) into (III) and also by the conversion of (VI) by the same reagent into (IX) and not into (V). Moreover, if compound (VI) were the 5 : 2′-anhydro-isomeride, acid hydrolysis would be expected to give a carboxylic acid, whereas actually it gives compound (IX).

Reduction of the nitro-acid (III) or the nitro-compound (IV) with alkaline hyposulphite (hydrosulphite) yields 2-(2′-*amino*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic acid* (VII), convertible by boiling acetic anhydride into the diacetyl derivative of (V). Unlike the lower homologue and its 4′-chloro-derivative, (VII) is converted into (VI) by refluxing with toluene in presence of phosphorus trichloride and is decomposed by refluxing with dilute sulphuric acid, so that compound (IX) cannot be obtained in the latter way. In agreement with its constitution as a derivative of an *o*-diamine, when compound (VII) is treated with nitrous acid, 2-(5′-*methyl*-1′ : 2′ : 3′-*benztriazolyl*)iso*indolinone*-3-*acetic acid* (VIII) is formed.

When 2 : 5-diketo-3-(2′-nitro-4′-methylphenyl)*iso*indolinopyrazolidocoline, or (II) or (III), is refluxed with aqueous-alcoholic sodium hydroxide until the violet solution becomes brown, hydrolysis occurs with formation of *m*-nitro-*p*-tolylhydrazine and phthalideacetic acid. The further action of alkali, however, converts these products respectively into 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole (Zincke and Schwarz, *Annalen*, 1900, **311**, 340) and *o*-carboxycinnamic acid, from which phthalideacetic acid is obtained by melting (Gabriel and Michael, *Ber.*, 1877, **10**, 2199). When 2-(2′-nitrophenylamino)*iso*indolinone-3-acetic acid (J., 1935, 1800) is hydrolysed similarly, *o*-carboxycinnamic acid is formed, but no 1-hydroxy-1 : 2 : 3-benztriazole was isolated. These degradation products are identical with authentic specimens. During the preparation of the latter we found that electrolytic reduction of phthalylacetic acid (Edwards, J., 1926, 816) gives phthalideacetic acid in low yield accompanied by much phthalic acid, whereas a good yield is obtained from *o*-cyano*allo*cinnamic acid (*loc. cit.*, p. 815) by hydrolysis with boiling dilute hydrochloric acid. In view of the wide range of m. p.'s of *o*-carboxycinnamic acid given in the literature (see p. 1103), we compared the various methods described for the preparation of

this compound. *o*-Carboxycinnamic acid, m. p. 205° with formation of phthalideacetic acid, m. p. 152°, is prepared conveniently and quantitatively by dissolving phthalideacetic acid in two molecular proportions of aqueous sodium hydroxide, evaporating the solution to dryness, and heating the resulting disodium β-(*o*-carboxyphenyl)-β-hydroxypropionate at 160° (cf. Leupold, *Ber.*, 1901, **34**, 2834).

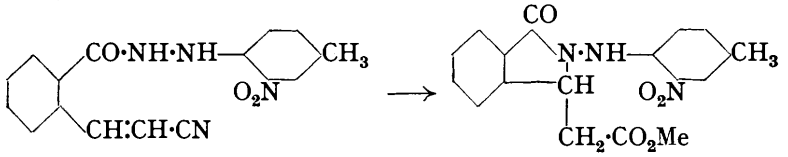
In connexion with the alkaline hydrolysis of *o*-cyanocinnamic acid (*allo* or *trans*), Edwards (*loc. cit.*) stated that refluxing with 10% sodium hydroxide solution for 2 hours yields *o*-carboxycinnamic acid, m. p. 182°, as does also similar treatment of *o*-carboxycinnamonitrile. The former statement is incorrect. The product indeed has m. p. 182°, but it cannot be *o*-carboxycinnamic acid, because it is a readily water-soluble nitrogen-containing monobasic acid, which melts unchanged without formation of phthalideacetic acid and depresses the m. p. of actual *o*-carboxycinnamic acid prepared as described above. Although some ammonia is evolved during the preparation, this is merely due to a side reaction, for the compound is recovered unaltered after boiling with sodium hydroxide solution or mineral acids. The compound is iso*indolinone*-3-*acetic acid* (X), formed from *o*-cyanocinnamic acid, *via* benzamide-2-β-acrylic acid, which cannot be isolated, as alkali converts it readily into (X) in an analogous manner to the conversion of (II) into (III).



(X.)

This view is supported by the fact that compound (X) is also obtained by a similar alkaline hydrolysis of *o*-carboxycinnamdiamide.

Phthalideacetic acid does not condense with *m*-nitro-*p*-tolylhydrazine to form 2-(2′-nitro-4′-methylphenylamino)*iso*indolinone-3-acetic acid, but the synthesis can be effected from *o*-carboxycinnamonitrile, *via* the acid chloride, which condenses readily with *m*-nitro-*p*-tolylhydrazine to form *benzo-2′-nitro-4′-methylphenylhydrazide-2-β-acrylonitrile* (XI). Compound (XI) is converted by methyl-alcoholic hydrogen chloride into methyl 2-(2′-nitro-4′-methylphenylamino)*iso*indolinone-3-acetate (XII), from which the free acid is obtained by careful hydrolysis with aqueous sodium hydroxide.

(XI.)


(XII.)

The synthetic acid and its methyl ester are identical with compound (III) and its methyl ester respectively.

Compound (I) is converted completely into *sodium hydrogen* 3-(2′-*nitro*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* by the action of aqueous sodium hydroxide for 2 days or by heating an aqueous solution under pressure. The resistance of sodium benzaldehydearylhydrazone-ω-sulphonate-2-β-acrylic acids (*e.g.*, I) to this ring closure appears to be related to the basicity of the particular arylamino-residue. Thus, compounds of type (I) derived from *o*-nitroamines are relatively stable in comparison with the *m*- and *p*-nitro-analogues.

1-*Hydroxy*-3-(2′-*nitro*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid*, prepared from the corresponding 1-sodium sulphonate in the usual way, does not form an *O*-acetate, but prolonged boiling with acetic anhydride and pyridine gives compound (IV), although in much lower yield than is obtained from the isomeride (III). Compound (IV) is hydrolysed by acids to compound (III) and again this is the only reaction by which we have succeeded in converting a phthalazine derivative into the isomeric *iso*indolinone derivative.

Iron and acetic acid reduce 1-hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid to the corresponding amino-acid, which readily passes into the

lactam. Unlike the behaviour of the lower homologue and its 4'-chloro-derivative (J., 1935, 1805), however, the lactam in the present series is so stable that boiling dilute mineral acids do not convert it into 2'-amino-3-phenyl-4'-methylphthalaz-1-one and acid reducing agents do not convert it into 5-methyl-*o*-benzylenebenziminazole. Attempts to prepare 2'-amino-3-phenyl-4'-methylphthalaz-1-one-4-acetic acid lactam or 2'-amino-3-phenyl-4 : 4'-dimethylphthalaz-1-one by the action of acid dichromate on the amino-acid or the lactam also failed.

On the other hand, *2'-nitro-3-phenyl-4'-methylphthalaz-1-one* is obtained in the usual way, although in much better yield than is the case with the lower homologue; the oxygen atom of the keto-group is methylated and the primary product combines with alcohol to form compounds which are sufficiently stable to enable their formulæ to be confirmed by analysis, but these compounds are merely decomposed by heat without formation of 4-keto-1-methoxy-3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine. Oxidation of 1-hydroxy-3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid with potassium permanganate (cf. J., 1935, 1811), however, yields 1 : 4-*diketo*-3-(*2'-nitro-4'-methylphenyl*)-*tetrahydrophthalazine* and the oxygen atom of the 1-keto-group of this compound can be alkylated *via* the silver salt. *2'-Nitro-3-phenyl-4 : 4'-dimethylphthalaz-1-one* also is obtained in the usual way, but its methylation product could not be purified. Reduction of 2'-nitro-3-phenyl-4'-methyl- and -4 : 4'-dimethyl-phthalaz-1-one with aqueous sodium sulphide does not give the corresponding amino-compounds.

Experimental.

Fuller details of preparation are given for the corresponding lower homologues (J., 1935, 1800).

Sodium Benzaldehyde-2'-nitro-4'-methylphenylhydrazone-ω-sulphonate-2-β-acrylic Acid (I).—A filtered solution of commercial 50% sodium β-naphthol-1-sulphonate (55 g.) in water (200 c.c.) was stirred rapidly at 0° into a solution of diazotised *m*-nitro-*p*-toluidine, prepared by pouring a cold solution of the base (15·2 g.) in concentrated sulphuric acid (40 c.c.) into a mixture of ice (200 g.) and water (100 c.c.), and then adding a solution of sodium nitrite (7·3 g.) in water (50 c.c.) during 15 minutes with good stirring. 2'-Nitro-4'-methylbenzene-2-naphthol-1-diazosulphonate separated as an orange precipitate. It was washed free from acid, mixed with cold water (140 c.c.), and a cold solution of anhydrous sodium carbonate (30 g.) in water (120 c.c.) added rapidly with good stirring. After 10 minutes, the resulting deep red solution of sodium 1-(2'-nitro-4'-methylbenzeneazo)-β-naphthaquinone-1-sulphonate, containing glistening plates of this compound in suspension, was stirred into a cold solution of sodium hydroxide (25 g.) in water (100 c.c.). The brown solution rapidly became violet and, after 1 minute, was acidified with concentrated hydrochloric acid within 1 minute by the addition of ethyl acetate to control frothing, then made alkaline with sodium carbonate, heated to 90° (charcoal), and filtered from 2'-nitro-4'-methylbenzeneazo-β-naphthol (2 g.). The cold filtrate was rendered faintly acid with hydrochloric acid and the acid *sodium* salt separated as an orange precipitate. It crystallised from alcohol or ethyl acetate in small, bright red needles (yield, 40 g.; 93·7% calculated on the *m*-nitro-*p*-toluidine) (Found: S, 7·45. $C_{17}H_{14}O_7N_3SNa$ requires S, 7·5%), readily soluble in hot water, and soluble in cold dilute sodium carbonate solution with a yellow colour and in cold concentrated sodium hydroxide solution with a bluish-violet colour, changing to yellowish-brown and then to orange on dilution. It is an orange acid dye, fugitive to light.

Benzo-2'-nitro-4'-methylphenylhydrazide-2-β-acrylic Acid (II) *and* 2-(*2'-Nitro-4'-methylphenylamino*)iso*indolinone-3-acetic Acid* (III).—The preceding sodium salt (I) (5 g.) was dissolved in boiling water (200 c.c.), concentrated hydrochloric acid (20 c.c.) added gradually, and boiling continued until evolution of sulphur dioxide had ceased (3 hours). The yellow crystalline precipitate was a mixture of the two isomerides (total yield, 3·4 g.; 85·1%) and contained approximately 40% of the open-chain compound (II), but the proportion varies with the conditions; estimation was based on matching the colour of a freshly prepared 0·004% solution of the mixture in cold 1% sodium hydroxide solution with that of a mixture of similar solutions of (II) (bluish-violet) and (III) (yellow).

Benzo-2'-nitro-4'-methylphenylhydrazide-2-β-acrylic acid was separated as the less soluble portion of such a mixture (25 g.) by heating with glacial acetic acid (70 c.c.), or alcohol, and filtering when hot; the residue (6 g.), crystallised rapidly without boiling from nitrobenzene–glacial acetic acid, formed orange-red prisms, m. p. 224—244° with ring closure and partial

decomposition (Found : C, 59·5; H, 4·4; N, 12·3. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%), soluble in cold dilute sodium carbonate solution with a deep bluish-violet colour, changing to blue on addition of acetone. It, or the above mixture containing it, by boiling with water, alcohol, toluene, glacial acetic acid or nitrobenzene, or by boiling the violet solution in 1% sodium carbonate until yellow, was converted into (III). The latter was prepared most conveniently, however, by dissolving 2 : 5-diketo-3-(2′-nitro-4′-methylphenyl)*iso*indolinopyrazolidocoline (IV) (20 g.) in warm concentrated sulphuric acid (200 c.c.) and pouring the solution on ice (800 g.) (yield, 20 g.; 94·7%).

2-(2′-*Nitro*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic acid* crystallised from ethyl acetate or alcohol in bright yellow prisms, m. p. 248° (Found : C, 59·4; H, 4·45; N, 12·15. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%), readily soluble in glacial acetic acid. It is insoluble in water, but dissolves readily in sodium carbonate solution with a yellow colour and in sodium hydroxide solution with a wine-red colour, and dissolves in cold concentrated sulphuric acid with an orange colour, being reprecipitated unaltered when this solution is diluted. It is also unaffected by refluxing with dilute sulphuric acid (b. p. 140°), and neither reacts with nitrous acid nor forms an *N*-methyl ether.

Derivatives of 2-(2′-*Nitro*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic Acid.*—The following derivatives were obtained whether (II) or (III) was used : The *methyl* ester crystallised from methyl alcohol in golden-yellow needles, m. p. 157° (Found : C, 61·0; H, 4·65. $C_{18}H_{17}O_5N_3$ requires C, 60·85; H, 4·8%), insoluble in sodium carbonate solution, but soluble in hot sodium hydroxide solution with a reddish-brown colour. The crude anilide, prepared in presence of toluene and phosphorus trichloride, contained some (IV), which was removed by hydrolysis by dissolving the product in concentrated sulphuric acid, pouring the solution on ice, and extracting (III) with sodium carbonate solution. The *anilide* crystallised from ethyl acetate in orange prisms, m. p. 258° (Found : C, 65·8; H, 4·75; N, 13·4. $C_{23}H_{20}O_4N_4$ requires C, 66·3; H, 4·8; N, 13·45%), insoluble in alkalis.

2 : 5-*Diketo*-3-(2′-*nitro*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (IV).—(a) The acid (III) (25 g.) was refluxed with acetic anhydride (110 c.c.) and pyridine (5 c.c.) for 3 hours; the product crystallised on cooling (yield, 22·5 g.; 95%). (b) The acid (2 g.) was refluxed with toluene (400 c.c.) and phosphorus trichloride (3 c.c.) for 1½ hours (yield, 1·5 g.; 79·2%). (c) The acid (2 g.) was refluxed with thionyl chloride (10 c.c.) for ½ hour, and thionyl chloride then removed under reduced pressure (yield, 1·6 g.; 84·5%). Benzo-2′-nitro-4′-methylphenylhydrazide-2-β-acrylic acid also can be used in these methods, but the yields are lower. The most convenient method of preparation is to reflux the above mixture of acids (II) and (III) (50 g.) with acetic anhydride (180 c.c.) and pyridine (10 c.c.) for 3 hours (yield, 33 g.; 70%).

2 : 5-*Diketo*-3-(2′-*nitro*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* crystallised from glacial acetic acid or ethyl acetate in pale yellow needles, m. p. 233° (Found : C, 63·15; H, 4·0; N, 13·05. $C_{17}H_{13}O_4N_3$ requires C, 63·15; H, 4·0; N, 13·0%), readily soluble in chloroform, insoluble in cold dilute mineral acids and alkalis, but soluble in concentrated sulphuric acid with an orange colour and (III) is precipitated on dilution of the solution. It does not react with *p*-nitrophenylhydrazine in glacial acetic acid solution.

Degradation of 2 : 5-*Diketo*-3-(2′-*nitro*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (IV), *or* (II) *or* (III), *with Aqueous-alcoholic Sodium Hydroxide.*—The nitro-compound (IV) (20 g.) was refluxed with a solution of sodium hydroxide (10 g.) in water (50 c.c.) and alcohol (50 c.c.) for 1 hour; the original deep reddish-violet colour of the solution changed to brown. After removal of alcohol under reduced pressure, the cold solution was acidified with hydrochloric acid ; the precipitate was collected, dissolved in hot dilute aqueous ammonia (charcoal), the solution filtered, and the cold filtrate acidified. The brown precipitate (16 g.) was separated into a readily soluble portion and a sparingly soluble residue by extraction with hot water (600 c.c.) and filtration of the hot liquid. The filtrate was concentrated and the crystalline product which separated on cooling was recrystallised several times from water; 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole was obtained in characteristic, colourless, hairy needles, m. p. 176° (decomp.) (yield, 0·5 g.) (Found : C, 55·6; H, 4·65; N, 28·6. Calc. for $C_7H_7ON_3$: C, 56·4; H, 4·7; N, 28·2%), readily soluble in hot water and in aqueous sodium hydroxide, and identical with a specimen prepared from ammonium *m*-nitro-*p*-tolylhydrazinesulphonate as described by Davies (J., 1922, **121**, 720). The above residue was crystallised repeatedly from dilute alcohol (charcoal); *o*-carboxycinnamic acid was obtained in colourless prisms, m. p. 205° with conversion into phthalideacetic acid, m. p. 152° (yield, 3 g.) (Found : C, 62·5; H, 4·2. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·15%) (Gabriel and Michael, *Ber.*, 1877, **10**, 2199, gave m. p. 173—175°; Ehrlich and Benedikt, *Monatsh.*, 1888, **9**, 527, gave m. p. 183—184°; Neunhoeffer and

Kölbel, *Ber.*, 1935, **68**, 258, gave m. p. 203°; and Böeseken and Lochmann von Königsfeldt, *Rec. trav. chim.*, 1935, **54**, 318, gave m. p. 183—184°), identical with an authentic specimen (see below). Identical derivatives were also obtained from both specimens, *viz.*, the diamide, which crystallised from dilute alcohol in colourless needles, m. p. 228° (Found: C, 63·05; H, 5·6; N, 15·15. Calc. for $C_{10}H_{10}O_2N_2$: C, 63·15; H, 5·25; N, 14·75%) (Gabriel, *Ber.*, 1916, **49**, 1611, gave m. p. 200—201°), and the *dianilide*, which crystallised from dilute alcohol (charcoal) in colourless needles, m. p. 172° (Found: C, 76·6; H, 5·5; N, 8·45. $C_{22}H_{18}O_2N_2$ requires C, 77·2; H, 5·25; N, 8·2%). Phthalideacetic acid, derived from our specimen of *o*-carboxycinnamic acid, crystallised from toluene (charcoal) in colourless prismatic needles, m. p. 152° (Found: C, 62·1; H, 4·2. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·15%), identical with a specimen prepared by electrolytic reduction of phthalylacetic acid as described by Edwards (J., 1926, 816); the amide, prepared from both specimens, crystallised from dilute alcohol in colourless needles, m. p. and mixed m. p. 184° (Found: C, 62·8; H, 4·8; N, 7·35. Calc. for $C_{10}H_9O_3N$: C, 62·85; H, 4·7; N, 7·3%) (Edwards, *loc. cit.*).

1-Hydroxy-6-methyl-1 : 2 : 3-benztriazole and *o*-carboxycinnamic acid were also isolated after similar treatment of the acids (II) and (III) with aqueous-alcoholic sodium hydroxide, but this decomposition did not occur when (II), (III) and (IV) were refluxed with aqueous-alcoholic sodium carbonate.

Phthalideacetic Acid.—*o*-Cyano*allo*cinnamic acid (17 g.), prepared from 1-nitroso-2-naphthol as described by Edwards (*loc. cit.*, p. 815), was dissolved in water (700 c.c.), concentrated hydrochloric acid (100 c.c.) added, and the solution boiled in a dish for 12 hours with additions of water and acid to replace losses by evaporation. The solution was then concentrated and filtered hot to remove any of the intermediate *o*-cyano-*trans*-cinnamic acid, which crystallised from alcohol (charcoal) in colourless needles, m. p. 250° (yield, 3·9 g.). Phthalideacetic acid separated from the acid filtrate on cooling and crystallised from toluene (charcoal) in colourless needles, m. p. 152° (yield, 11·5 g.; 60·1%).

iso*Indolinone*-3-*acetic Acid* (X).—*o*-Cyanocinnamic acid (*allo* or *trans*) (10 g.) was refluxed with 10% sodium hydroxide solution (60 c.c.) for 3 hours, during which some ammonia was evolved owing to partial hydrolysis. The solution was cooled, acidified with hydrochloric acid, and left over-night until the precipitate had separated completely. iso*Indolinone*-3-*acetic acid* crystallised from water in colourless prismatic needles, m. p. 182° and remelting at 182° (yield, 9·5 g.; 86%) (Found: N, 7·5. $C_{10}H_9O_3N$ requires N, 7·3%), readily soluble in water, alcohol, toluene, and dilute alkalis. It was also obtained by refluxing *o*-carboxycinnamdiamide (1·5 g.) with 10% sodium hydroxide solution (40 c.c.) for 1½ hours. *iso*Indolinone-3-acetic acid was unaltered by refluxing with dilute hydrochloric acid for 8 hours or by heating with concentrated sulphuric acid at 100° for 1 hour; it did not react satisfactorily with phosphorus pentachloride, but was converted neatly into the acid chloride by thionyl chloride. iso*Indolinone*-3-*acetamide* crystallised from water (charcoal) in colourless needles, m. p. 221° (Found: C, 62·95; H, 5·1; N, 14·55. $C_{10}H_{10}O_2N_2$ requires C, 63·15; H, 5·25; N, 14·7%), readily soluble in water and in organic solvents. It is not formed by melting *o*-carboxycinnamdiamide or by heating with nitrobenzene, the diamide being recovered unaltered after either treatment.

o-*Carboxycinnamic Acid.*—The methods that have been described for the preparation of this acid (see the literature quoted above in connexion with the m. p. of this acid) were compared. The following method was found to be best: A solution of phthalideacetic acid (10 g.) in aqueous sodium hydroxide (2 mols.) was evaporated to dryness, and the resulting disodium β-(*o*-carboxyphenyl)-β-hydroxypropionate heated in an air-oven at 160° for 6 hours. The product was dissolved in cold water, and the solution precipitated with acid. *o*-Carboxycinnamic acid crystallised from dilute alcohol (charcoal) in colourless prismatic needles, m. p. 205° with conversion into phthalideacetic acid, m. p. 152° (yield, 10 g.; 100%).

Synthesis of 2-(2′-*Nitro*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic Acid* (III).—*o*-Carboxycinnamonitrile (1 g.), prepared from phthalideacetamide *via* phthalideacetonitrile as described by Edwards (*loc. cit.*), and phosphorus pentachloride (1·25 g.) were heated to 100° in an oil-bath, and then phosphorus oxychloride was removed under reduced pressure. The colourless solid residue of the acid chloride (Borsche and Sander, *Ber.*, 1915, **47**, 2825) was dissolved in chloroform (20 c.c.), and the solution filtered into a hot solution of excess of *m*-nitro-*p*-tolylhydrazine (2 g.) in chloroform (50 c.c.); an orange precipitate separated immediately. The mixture was refluxed for 10 minutes, water (100 c.c.) and concentrated hydrochloric acid (3 c.c.) then added, chloroform removed, and the reddish-brown precipitate (yield, 1·5 g.; 80·6%) filtered off and washed with water. *Benzo*-2′-*nitro*-4′-*methylphenylhydrazide*-2-β-*acrylonitrile* (XI) crystallised from toluene in orange prismatic needles, m. p. 201°, containing toluene of crystallisation which

could not be removed completely by heat (Found in material dried at 120° : C, 66·4; H, 5·2; N, 15·5. $C_{17}H_{14}O_3N_4,\frac{1}{2}C_7H_8$ requires C, 66·85; H, 4·9; N, 15·2%), sparingly soluble in most organic solvents and very slightly soluble in hot aqueous sodium hydroxide with a wine-red colour and odour of toluene.

Compound (XI) (1 g.) was suspended in dry methyl alcohol (40 c.c.) and saturated with dry hydrogen chloride at 0°. After 12 hours, the dark orange solution was refluxed for 2 hours and then concentrated. The orange-brown precipitate which separated on cooling crystallised from methyl alcohol (charcoal) in golden-yellow needles, m. p. and mixed m. p. 157°, identical with methyl 2-(2′-nitro-4′-methylphenylamino)*iso*indolinone-3-acetate (see p. 1103) (yield, 0·25 g.; 22·7%). Careful hydrolysis of this ester (XII) with aqueous sodium hydroxide and crystallisation of the alkali-soluble product from glacial acetic acid gave 2-(2′-nitro-4′-methylphenylamino)*iso*indolinone-3-acetic acid, yellow prisms, m. p. and mixed m. p. with (III) 248°.

2 : 5-*Diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (V).—The nitro-compound (IV) (10 g.) was dissolved in boiling glacial acetic acid (100 c.c.) and water (25 c.c.), and iron powder (5 g.) added gradually so that steady ebullition was maintained. The mixture was then refluxed for ½ hour, filtered hot, and the filtrate poured into water (1500 c.c.); pale green felted needles separated. 2 : 5-*Diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* crystallised from ethyl acetate (charcoal) in colourless feathery needles, m. p. 233° (yield, 8 g.; 88·2%) (Found : C, 69·45; H, 5·1; N, 14·55. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1; N, 14·3%), soluble in most organic solvents and in acids, and diazotisable. It does not react with *p*-nitrophenylhydrazine. Similar conditions to those used for the monoacetylation of the lower homologue (*loc. cit.*) resulted in a difficulty separable mixture of the more soluble mono- and the less soluble di-acetyl derivative. The *diacetyl* derivative, prepared by refluxing (2·5 g.) with acetic anhydride (25 c.c.) and pyridine (2 c.c.) for 6 hours, crystallised from alcohol in colourless glistening plates, m. p. 194° (Found : C, 66·8; H, 5·1; N, 11·15. $C_{21}H_{19}O_4N_3$ requires C, 66·85; H, 5·05; N, 11·15%).

2 : 2′-*Anhydro*-2 : 5-*diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (VI).—(a) A solution of the amino-compound (V) (5 g.) in dilute sulphuric acid (1 : 1) (10 c.c.) was heated to b. p., then cooled at once, and water (100 c.c.) added. The *sulphate* which separated crystallised from alcohol (charcoal) in almost colourless needles (3·6 g.), m. p. 269° (decomp.) [Found : N, 13·15. $(C_{17}H_{13}ON_3)_2,H_2SO_4$ requires N, 12·95%], and was basified with sodium carbonate solution (yield, 3 g.; 63·7%). (b) The amino-compound (5 g.) was refluxed with toluene (300 c.c.) and phosphorus trichloride (2 c.c.) for 4 hours (yield, 1·2 g.; 25·5%). It was also obtained by method (b) from the amino-acid (VII) (yield, 15%) and from the lactam (IX) (yield, 21%).

2 : 2′-*Anhydro*-2 : 5-*diketo*-3-(2′-*amino*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* crystallised from ethyl acetate in large colourless prisms, m. p. 242° (Found : C, 73·95; H, 4·65; N, 14·9. $C_{17}H_{13}ON_3$ requires C, 74·15; H, 4·7; N, 15·25%), soluble in most organic solvents and in moderately concentrated mineral acids, but insoluble in alkalis. The *picrate* crystallised from alcohol in bright yellow needles, m. p. 239° (Found : C, 54·5; H, 3·0; N, 17·25. $C_{23}H_{16}O_8N_6$ requires C, 54·75; H, 3·15; N, 16·7%), and was also obtained directly, but more slowly, from (V); the base (VI) was recovered on warming the picrate with aqueous ammonia.

2-(2′-*Amino*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic Acid* (VII).—The nitro-acid (III) (10 g.), moistened with alcohol, was dissolved in a solution of sodium hydroxide (10 g.) in water (300 c.c.), and hyposulphite (about 20 g.) added at 80° until the deep red colour had changed to pale yellow. The solution was filtered (charcoal), the excess of alkali in the cold filtrate neutralised very carefully with dilute acetic acid, and the white precipitate filtered off, washed with cold water, and dried in a vacuum over calcium chloride (yield, 6·6 g.; 72·3%). It was also obtained, but in lower yield, by a similar reduction of (IV).

2-(2′-*Amino*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic acid* crystallised from dilute alcohol in pale greyish, prismatic needles, becoming green at 180° and melting at 185° (decomp.) (Found : C, 65·2; H, 5·5; N, 13·3. $C_{17}H_{17}O_3N_3$ requires C, 65·6; H, 5·45; N, 13·5%), soluble in most organic solvents, the solutions soon becoming green owing to decomposition, with the result that crystallisation must be carried out rapidly. It is readily soluble in cold dilute mineral acids and alkalis. It does not form an acetyl derivative, but yields 2 : 5-diketo-3-(2′-diacetamido-4′-methylphenyl)*iso*indolinopyrazolidocoline (above). The product of an attempt to prepare an anilide in presence of phosphorus trichloride and toluene was (VI). Methylation with methyl alcohol and hydrogen chloride gave the *methyl ester hydrochloride*, pale greyish, prismatic needles, m. p. 204° (decomp.) (Found : N, 11·6; Cl, 9·75. $C_{18}H_{19}O_3N_3$,HCl requires N, 11·6; Cl, 9·8%), sparingly soluble in hot water, insoluble in alkalis, and converted into the rather unstable base of the methyl ester by addition of sodium hydroxide to a hot aqueous solution.

2-(5′-*Methyl*-1′ : 2′ : 3′-*benztriazolyl*)iso*indolinone*-3-*acetic Acid* (VIII).—The amino-acid (VII) (10 g.) was dissolved in cold 10% sulphuric acid (200 c.c.), and a solution of sodium nitrite (2·3 g.) in water (20 c.c.) added at 0°. The yellow precipitate rapidly became pink, and after 1 hour was filtered off and washed with water. 2-(5′-*Methyl*-1′ : 2′ : 3′-*benztriazolyl*)iso*indolinone*-3-*acetic acid* crystallised from dilute alcohol (charcoal) in almost colourless needles, m. p. 253° (yield, 9·6 g.; 92·7%) (Found: N, 17·65. $C_{17}H_{14}O_3N_4$ requires N, 17·4%), readily soluble in alkalis and insoluble in dilute mineral acids. The *amide* crystallised from dilute alcohol in colourless needles, m. p. 214° (Found: C, 63·4; H, 4·8; N, 21·6. $C_{17}H_{15}O_2N_5$ requires C, 63·55; H, 4·65; N, 21·8%), insoluble in alkalis and dilute mineral acids. The *anilide* crystallised from dilute alcohol in colourless needles, m. p. 221° (Found: C, 68·9; H, 4·65; N, 17·9. $C_{23}H_{19}O_2N_5$ requires C, 69·5; H, 4·8; N, 17·6%). The *methyl* ester, obtained either by methylating (VIII) with methyl alcohol and hydrogen chloride or by the action of nitrous acid on the methyl ester of (VII), could not be purified or crystallised (Found: N, 16·0. $C_{18}H_{16}O_3N_4$ requires N, 16·65%).

2-(2′-*Amino*-4′-*methylphenylamino*)iso*indolinone*-3-*acetic Acid Lactam* (IX).—The sulphate of 2 : 2′-anhydro-2 : 5-diketo-3-(2′-amino-4′-methylphenyl)*iso*indolinopyrazolidocoline (3 g.) was refluxed with dilute sulphuric acid (1 : 1) (20 c.c.) for 3 hours; the brown solution was cooled to 0°, diluted with water (50 c.c.), and neutralised with ammonia with ice-cooling, and the precipitate crystallised (yield, 1·2 g.; 44·2%). It was also obtained (yield, 16%) by refluxing 2 : 5-diketo-3-(2′-amino-4′-methylphenyl)*iso*indolinopyrazolidocoline with dilute sulphuric acid under the same conditions, but it was not obtained by the action of mineral acids on 2-(2′-amino-4′-methylphenylamino)*iso*indolinone-3-acetic acid, although many experiments were carried out with both sulphuric and hydrochloric acid under a variety of conditions, the products being intractable resins.

2-(2′-*Aminophenylamino*)iso*indolinone*-3-*acetic acid lactam* crystallised from ethyl acetate in colourless feathery needles, m. p. 231° (Found: C, 69·6; H, 5·2; N, 14·55. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1; N, 14·35%), readily soluble in cold dilute mineral acids and insoluble in alkalis. The *picrate* crystallised from alcohol in yellow needles, m. p. 226° (Found: C, 52·9; H, 3·35; N, 16·3. $C_{23}H_{18}O_9N_6$ requires C, 52·85; H, 3·45; N, 16·1%); the base (IX) was recovered by warming the picrate with aqueous ammonia.

Sodium Hydrogen 3-(2′-*Nitro*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*.—(a) A solution of sodium 1-(2′-nitro-4′-methylbenzeneazo)-β-naphthaquinone-1-sulphonate in sodium hydroxide, prepared exactly as described under sodium benzaldehyde-2′-nitro-4′-methylphenylhydrazone-ω-sulphonate-2-β-acrylic acid (I) (p. 1102), instead of being acidified after 1 minute, was kept at room temperature for 2 days and then acidified. After separation from 2′-nitro-4′-methylbenzeneazo-β-naphthol (1·4 g.), the product was isolated in the usual manner (yield, 41 g.; 96%, calculated on the *m*-nitro-*p*-toluidine). (b) A solution of sodium benzaldehyde-2′-nitro-4′-methylphenylhydrazone-ω-sulphonate-2-β-acrylic acid (42·7 g.) in 20% aqueous sodium hydroxide (500 c.c.) was kept at room temperature for 2 days (yield, 38·4 g.; 89·9%), or the sodium salt (2·5 g.) was heated with water (15 c.c.) in a sealed tube at 150° for 6 hours (yield, 2·1 g.; 84%). The identity of the products was confirmed by conversion into 1-hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid.

Sodium hydrogen 3-(2′-*nitro*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* crystallised from dilute alcohol in brownish-yellow needles, which became redder on drying, or from ethyl acetate in orange-red needles (Found: S, 7·0. $C_{17}H_{14}O_7N_3SNa$ requires S, 7·5%), readily soluble in hot water, but not very soluble in organic solvents. It is a yellowish-orange acid dye, fugitive to light.

1-*Hydroxy*-3-(2′-*nitro*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid*.—A solution of the preceding sodium hydrogen salt (20 g.) in water (800 c.c.) was boiled, and concentrated hydrochloric acid (80 c.c.) added gradually until evolution of sulphur dioxide had ceased. The *acid* separated in yellowish-brown crystals; recrystallised from ethyl acetate or glacial acetic acid, it formed large yellow prisms, m. p. 233° (yield, 14·5 g.; 90·8%) (Found: C, 59·2; H, 4·45; N, 12·25. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%), almost insoluble in benzene or toluene. It dissolves readily in cold dilute sodium carbonate or hydroxide solution with a reddish-brown or reddish-violet colour respectively, and dissolves in cold concentrated sulphuric acid with an orange colour, being reprecipitated unaltered when this solution is diluted.

The *methyl* ester crystallised from methyl alcohol in long yellow needles, m. p. 169° (Found: C, 60·6; H, 4·7; N, 12·15. $C_{18}H_{17}O_5N_3$ requires C, 60·85; H, 4·8; N, 11·8%), insoluble in sodium carbonate solution, but soluble in hot sodium hydroxide solution with a reddish-violet colour. The *N*-methyl ether, 1-*keto*-3-(2′-*nitro*-4′-*methylphenyl*)-2-*methyltetrahydrophthalazine*-

4-*acetic acid*, crystallised from methyl alcohol or glacial acetic acid in orange prisms, m. p. 187—188° (decomp.) (Found : C, 60·6; H, 4·9; N, 12·2. $C_{18}H_{17}O_5N_3$ requires C, 60·85; H, 4·8; N, 11·8%), soluble in cold dilute sodium carbonate or hydroxide solution with an orange or reddish-brown colour respectively.

2 : 5-*Diketo*-3-(2′-*nitro*-4′-*methylphenyl*)iso*indolinopyrazolidocoline* (IV).—1-Hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) was refluxed with acetic anhydride (30 c.c.) and pyridine (2 c.c.) for 66 hours; the product crystallised on cooling; recrystallised from glacial acetic acid, it formed pale yellow needles, m. p. and mixed m. p. 233° (yield, 2·9 g.; 30·6%).

1-*Hydroxy*-3-(2′-*amino*-4′-*methylphenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic Acid and its Lactam.*—Iron powder (7 g.) was added gradually during 10 minutes to a boiling solution of 1-hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) in glacial acetic acid (100 c.c.) and water (80 c.c.); the mixture was boiled for 20 minutes longer (charcoal) and filtered hot. The filtrate was either (a) poured on ice (250 g.), mainly the acid separating (yield, 7 g.; 76·8%), or (b) added to boiling water (100 c.c.), boiled for 10 minutes (charcoal), and filtered, and the filtrate allowed to crystallise. In the latter case, the crystalline product was mainly the lactam and a little of the acid; a further quantity of the acid was isolated by partial neutralisation of the filtrate with sodium carbonate solution (yield of lactam, 4·3 g., and of acid, 2·2 g.; 74·1%). The lactam was best prepared by dissolving the acid in aqueous sodium carbonate, then rendering the solution faintly acid with dilute hydrochloric acid and boiling, almost colourless prisms progressively separating. The acid, a greyish-white powder, m. p. 180—200° (decomp.) *without* conversion into the lactam (cf. J., 1935, 1805), could not be purified, as heating with water, aqueous mineral acids or organic solvents converted it into the lactam. The *lactam* crystallised from alcohol in almost colourless prisms, m. p. 282—284° (Found : C, 69·3; H, 5·3; N, 14·6. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1; N, 14·3%), insoluble in cold alkalis, but soluble in boiling aqueous sodium hydroxide with a pale yellow colour and reprecipitated unaltered on acidification. Unlike the lower homologue and its 4′-chloro-derivative (*loc. cit.*), the lactam is remarkably stable to mineral acids and was recovered unaltered after refluxing with dilute sulphuric acid (b. p. 140°), or with concentrated hydrochloric acid, for 3 hours. 2′-Amino-3-phenyl-4′-methylphthalaz-1-one could not be obtained from either the acid or its lactam even by heating with dilute sulphuric acid (1 : 1) in a sealed tube for 120° for 3 hours. Moreover, 5-methyl-*o*-benzylenebenziminazole could not be obtained from the acid by boiling with stannous chloride, tin and hydrochloric acid, or with zinc dust and dilute sulphuric acid, the products being intractable resins. Neither the acid nor its lactam could be converted into 2′-amino-3-phenyl-4′-methylphthalaz-1-one-4-acetic acid lactam or 2′-amino-3-phenyl-4 : 4′-dimethylphthalaz-1-one by the action of acid dichromate (cf. J., 1935, 1807); a substance, colourless needles, m. p. 311—313° (decomp.), was obtained, but this requires further investigation.

2′-*Nitro*-3-*phenyl*-4′-*methylphthalaz*-1-*one*.—A solution of 1-hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) in concentrated sulphuric acid (45 c.c.) was diluted carefully with water (50 c.c.) and refluxed for 1½ hours; the dark brown solution was then diluted with water (100 c.c.), boiled (charcoal), and filtered, and the filtrate kept for 1 day. The brown crystalline sulphate was filtered off and neutralised by grinding with warm aqueous ammonia. A further quantity, but less pure, was isolated by neutralising the filtrate from the sulphate with aqueous sodium hydroxide. 2′-*Nitro*-3-*phenyl*-4′-*methylphthalaz*-1-*one* crystallised from methyl alcohol in yellow prisms, m. p. 256—258° (yield, 4·3 g.; 52·2%) (Found : C, 64·4; H, 4·2; N, 15·2. $C_{15}H_{11}O_3N_3$ requires C, 64·05; H, 3·9; N, 14·95%), soluble in warm sodium hydroxide solution with a reddish-brown colour and soluble in aqueous mineral acid. Reduction with aqueous sodium sulphide or hydrosulphide gave intractable resins.

Action of methyl sulphate. 2′-Nitro-3-phenyl-4′-methylphthalaz-1-one (2 g.) in dry nitrobenzene (30 c.c.) was heated at 120°, and methyl sulphate (1·5 g.) added slowly. After ½ hour, the orange product was isolated (cf. J., 1928, 2554). The 1-*methoxy*-derivative combined with methyl alcohol and then crystallised in orange-yellow needles, m. p. 119—121° (Found : C, 63·0; H, 5·0; OMe, 19·2. $C_{17}H_{17}O_4N_3$ requires C, 62·4; H, 5·2; OMe, 18·95%), and combined with ethyl alcohol and then crystallised in orange-yellow prismatic needles, m. p. 115—117° (Found : C, 63·2; H, 5·6; OMe and OEt, 22·15. $C_{18}H_{19}O_4N_3$ requires C, 63·3; H, 5·6; OMe and OEt, 22·3%). Both compounds are decomposed by heat, but without formation of 4-keto-1-methoxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine.

1 : 4-*Diketo*-3-(2′-*nitro*-4′-*methylphenyl*)*tetrahydrophthalazine*.—1-Hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) was oxidised with aqueous potassium permanganate in a similar manner to the 4′-nitrophenyl-analogue (J., 1935, 1811). 1 : 4-

Diketo-3-(2′-nitro-4′-methylphenyl)tetrahydrophthalazine crystallised from glacial acetic acid in yellow prisms, m. p. 286—288° (yield, 3 g.; 34·4%) (Found : C, 60·6; H, 3·8; N, 14·2. $C_{15}H_{11}O_4N_3$ requires C, 60·6; H, 3·7; N, 14·1%), soluble in aqueous alkalis with a yellow colour. The yellow silver salt (2 g.) was refluxed with ethyl iodide (2 g.) and dry benzene (20 c.c.) for ¾ hour. *4-Keto-1-ethoxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine* crystallised from benzene in pale yellow, glistening plates, m. p. 185°, containing benzene of crystallisation, gradually lost in air, the crystals then becoming opaque (Found in material dried at 100° : C, 62·7; H, 4·55; N, 13·2. $C_{17}H_{15}O_4N_3$ requires C, 62·75; H, 4·6; N, 12·9%).

2′-Nitro-3-phenyl-4 : 4′-dimethylphthalaz-1-one.—A solution of 1-hydroxy-3-(2′-nitro-4′-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (10 g.) in cold concentrated sulphuric acid (75 c.c.) was poured on ice (100 g.), and finely powdered potassium dichromate (4 g.) added at 15—20° during 1 hour with good agitation. After 2 hours' further stirring, the mixture was left over-night at room temperature and then neutralised with concentrated aqueous sodium hydroxide with ice-cooling. The orange sticky product which separated was ground with warm aqueous ammonia and solidified after 2—3 hours; it was filtered off, ground with dilute sodium carbonate solution, and then washed with water. *4′-Nitro-3-phenyl-4 : 4′-dimethylphthalaz-1-one* crystallised from methyl alcohol in pale yellow, prismatic needles, m. p. 236° (yield, 6·5 g.; 75·1%) (Found : C, 65·1; H, 4·35; N, 14·0. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·4; N, 14·2%), soluble in aqueous mineral acid, and soluble in warm dilute sodium hydroxide solution with a reddish-brown colour, converted into deep violet on addition of acetone, this being a characteristic property of 2′-nitro-3-aryl-4-methylphthalaz-1-ones. Reduction with aqueous or aqueous-alcoholic sodium sulphide or hydrosulphide gave intractable resins.

Action of methyl sulphate. 2′-Nitro-3-phenyl-4 : 4′-dimethylphthalaz-1-one (1·2 g.) and methyl sulphate (1·2 g.) were stirred and heated to 50°; the yellow solution was kept at 45° for ¼ hour, then added to boiling water (100 c.c.), boiled for 1 minute, and cooled, and concentrated sodium acetate solution added to remove mineral acid. After several hours, the cloudy solution was filtered, and the filtrate basified with sodium carbonate; the yellow gelatinous precipitate soon changed to a deep red resin. Although the crude material contained a methoxy-group, it decomposed during attempted purification from organic solvents. By addition of perchloric acid to a fresh diluted methylation mixture, a perchlorate was obtained, but it also was unstable and decomposed on attempted crystallisation.

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