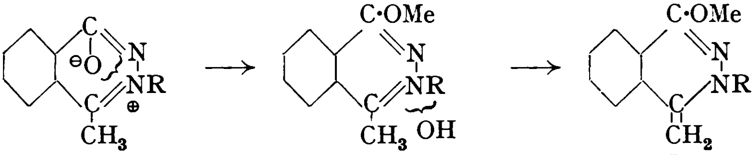
380. *A Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part XVI. The Constitution and Reactions of 1-Methoxy-3-(4'- and 3'-nitroaryl)-4-methylene-3 : 4-dihydrophthalazines.*

By F. M. Rowe and H. J. Twitchett.

The methylated bases of 3-nitroarylphthalaz-1-ones combine with alcohols and the resulting compounds in three instances are converted by heat into corresponding 4-keto-1-methoxy-3-(nitroaryl)-3 : 4-dihydrophthalazines; the constitution of the latter has been confirmed by synthesis (J., 1935, 1808).

The oxygen atom of the 1-keto-group of 4'-nitro-3-aryl-4-methylphthalaz-1-ones (I) also can be methylated with methyl sulphate, and coloured bases (of which II is probably the precursor) isolated. These methylated bases, however, do not combine with alcohols and after recrystallisation from ethyl acetate or alcohols are merely decomposed by heat. The red crystalline substances contain 1 molecule of water less than is required by (II) and are considered to be 1-methoxy-3-(4'-nitroaryl)-4-methylene-3 : 4-dihydrophthalazines (III; R = 4'-nitrophenyl, 2' : 6'-dibromo- or -dichloro-4'-nitrophenyl, 2'-chloro-4'-nitrophenyl, or 4'-nitro-2'-methylphenyl) (J., 1931, 1068, 1077; 1932, 13, 474). Compounds (III) are reconverted into (I) by demethylation.



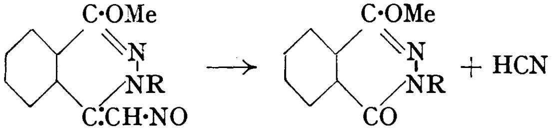
(I.) (II.) (III.)

Although methyl sulphate reacts in other cases (I; R = 3'- or 2'-nitrophenyl, 4'-chloro-2'-nitrophenyl, or 2'-nitro-4'-methylphenyl) (J., 1931, 1919; 1935, 1798; this vol., p. 1102), the products resist crystallisation, and in one instance only (I; R = 2'-bromo-4'-nitrophenyl) (J., 1935, 1135) methylation does not occur. The preparation of compounds (III; R = 4'-nitrophenyl, 2' : 6'-dichloro-4'-nitrophenyl, or 3'-nitrophenyl) has now been re-examined, but the main object of the present investigation was to confirm the constitution of these compounds by means of reactions characteristic of compounds containing an external methylene group.

Originally compounds (I) were methylated in nitrobenzene solution with methyl sulphate at 130°, but closer examination has revealed that this method results in the simultaneous formation of the corresponding 4-keto-1-methoxy-3-(nitroaryl)-3 : 4-dihydrophthalazine. This side reaction is avoided, however, by omitting nitrobenzene and it is also preferable to use a lower temperature, *viz.*, 50—70° according to the nature of the compound. On the addition of sodium carbonate to an aqueous solution of the methosulphate, an orange-yellow gelatinous precipitate separates and this is probably the ammonium hydroxide (II), but it coagulates almost immediately to the red ψ-base (III). Thus the molecule of water is lost at this stage and not during subsequent crystallisation.

Most compounds containing external methylene groups are obtained as intractable resinous materials or liquids which become coloured and resinify on exposure to light and air, and even such crystalline compounds as those described by Mills and Raper (J., 1925, **127**, 2466) and Rosenhauer (*Ber.*, 1926, **59**, 946) can be preserved for only a few days without decomposition. The 1-methoxy-3-(4'-nitroaryl)-4-methylene-3 : 4-dihydrophthalazines, therefore, appear to be unique in that they crystallise readily and can then be preserved indefinitely without decomposition. This high stability, however, is allied with low basicity and reactivity; thus, only the *perchlorates* have been prepared pure, as other salts are low-melting and uncrystallisable, and the reactions now recorded in which a perchlorate is used do not occur if another crude salt is used in its place. When the perchlorates are used, many of the products possess low solubility and their analysis is difficult, because, although the compounds are generally stable at their melting point, decomposition may occur explosively at a slightly higher temperature.

Kuhn, Winterstein, and Balser (*Ber.*, 1930, **63**, 3178) nitrosated 1 : 3 : 3-trimethyl-2-methyleneindoline and isolated almost quantitatively 2-oximinomethyl-3 : 3-dimethylindolenine methoperchlorate, which is decomposed by boiling acetic anhydride with formation of hydrogen cyanide and 1 : 3 : 3-trimethylindolinone. When compound (III; R = 4′-nitrophenyl) is treated with sodium nitrite under similar conditions, 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine is deposited gradually and hydrogen cyanide is evolved. Thus, nitrosation does occur slowly, but the product is



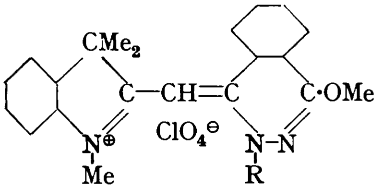
unstable and decomposes more readily than the corresponding indoline derivative. Compound (III) is also converted rapidly into 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine by boiling with *p*-nitrosodimethylaniline in alcoholic solution.

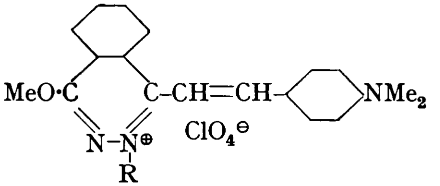
Mills and Raper (*loc. cit.*) considered that ψ-bases containing external methylene groups should combine with benzyl iodide to form ammonium salts in which the benzyl residue is attached, not to the nitrogen atom, but to the methylene group. The products they obtained from the ψ-base of quinaldine ethiodide were dibenzylquinaldine ethiodide and quinaldine ethiodide, and they established the sequence of reactions leading to this result (cf. also Mills and Akers, J., 1925, **127**, 2475). Compounds (III; R = 4′- or 3′-nitrophenyl) condense with benzyl iodide, the reaction being more rapid and complete with the 3′-nitro-compound. The products, however, are 1-*methoxy*-3-(4′- and 3′-*nitrophenyl*)-4-(β-*phenylethyl*)*phthalazinium iodides* and we were unable to prepare dibenzyl derivatives by the further action of excess of benzyl iodide on them in presence of potassium acetate.

Kuhn, Winterstein, and Balser (*loc. cit.*) could not condense 1 : 3 : 3-trimethylindolinone with 1 : 2 : 3 : 3-tetramethylindoleninium salts, and we also failed to condense 4-keto-1-methoxy-3-(4′- or 3′-nitrophenyl)-3 : 4-dihydrophthalazine with *cyclo*ammonium salts containing reactive methylene groups.

Kuhn, Winterstein, and Balser (*loc. cit.*) condensed 1 : 3 : 3-trimethyl-2-methyleneindoline with 2-oximinomethyl-3 : 3-dimethylindolenine methoperchlorate in acetic anhydride solution at 80—90° with elimination of hydrogen cyanide and formation of the monomethin derivative, indolenine-yellow. Compound (III) condenses similarly with 2-oximinomethyl-3 : 3-dimethylindolenine methoperchlorate with elimination of hydrogen cyanide and formation of the easily hydrolysed (1 : 3 : 3-*trimethyl*-2-*indolenino*)(1′-*methoxy*-3′-p-*nitrophenyl*-3′ : 4′-*dihydro*-4′-*phthalazino*)*cyanine perchlorate* (IV). The crude *m*-nitrophenyl isomeride was isolated only as a red viscous oil.

The preparation of symmetrical phthalazinocyanines from the perchlorates of (III; R = *p*- or *m*-nitrophenyl) was attempted by the method of Fisher and Hamer (J., 1930, 2502), but the development of a deep reddish-brown to red colour was the sole evidence of the formation of a monomethin derivative and the unaltered perchlorate was the only recognisable compound isolated from the resinous product. This result is perhaps not surprising in view of the instability of the unsymmetrical compound (IV).

(IV.)




(V.)

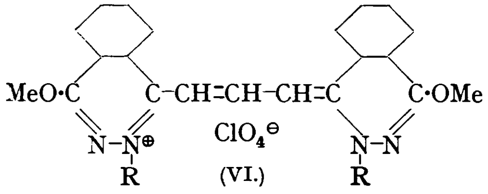
The inferior reactivity of compounds (III; R = 4′-nitrophenyl, 2′ : 6′-dichloro-4′-nitrophenyl, or 3′-nitrophenyl) in comparison with quinaldine derivatives is shown by the fact that the perchlorates of the former do not condense with *p*-dimethylaminobenzaldehyde in boiling alcoholic solution in presence of piperidine. Condensation occurs readily, however, in hot acetic anhydride solution with formation of 1-*methoxy*-3-(4′-*nitro*-, 2′ : 6′-*dichloro*-4′-*nitro*-, and 3′-*nitro-phenyl*)-4-p-*dimethylaminostyrylphthalazinium perchlorate* (V), although we obtained no analogous compounds by the use of benzaldehyde, or its dichloro-, nitro-, or hydroxy-derivatives under similar conditions.

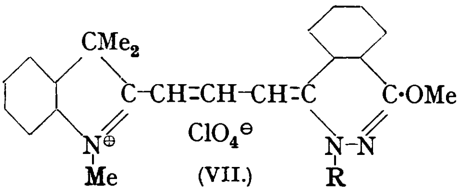
Attempts to prepare, from the perchlorates of (III) by the action of glyoxal in pyridine or acetic anhydride solution, divinylene compounds analogous to those described by Hamer, Heilbron, Reade, and Walls (J., 1932, 255) were unsuccessful.

Kaufmann and Vallette (*Ber.*, 1912, **45**, 1736) condensed *p*-nitrosodimethylaniline with quinaldine ethiodide and obtained the *p*-dimethylamino-anil, and other anils of this type have been described by Smith (J., 1923, **123**, 2288) and Bloch and Hamer (*Phot. J.*, 1930, **70**, 374). When the perchlorates of (III; R = 4′- or 3′-nitrophenyl) are warmed with *p*-nitrosodimethylaniline in acetic anhydride solution, or in alcoholic solution containing a little acetic anhydride, a transient deep blue colour apparently indicates the formation of the *p*-dimethylamino-anil. A little of a dark blue, amorphous powder was isolated in the case of the 4′-nitro-compound by cooling the reaction mixture immediately the blue colour appeared, but this substance could not be purified. No *p*-dimethylamino-anils of trialkylindoleninium salts are described in the literature and our attempts to prepare them failed.

The perchlorate of (III; R = 4′-nitrophenyl) does not react with formaldehyde in alcoholic solution containing sodium hydroxide, whereas alkyl salts of quinaldine under similar conditions yield deep blue solutions. Neither (III) nor its perchlorate reacts in boiling 90% formic acid solution (cf. Kuhn and Winterstein, B.P. 328,357), a method claimed to give carbocyanine dyes when other processes fail. When a mixture of (III; R = 4′- or 3′-nitrophenyl) and its perchlorate in acetic anhydride solution is boiled with ethyl orthoformate or, better, diphenylformamidine, however, condensation is rapid and *bis*-(1-*methoxy*-3-p- and -m-*nitrophenyl*-3 : 4-*dihydro*-4-*phthalazino*)*carbocyanine perchlorates* (VI) are obtained. Numerous attempts to prepare from equimolecular proportions of the perchlorate of (III) and diphenylformamidine, the condensation product analogous to the ω-anilinovinyl compounds described by Imperial Chemical Industries Ltd., Piggott, and Rodd (B.P. 344,409) and Ogata (*Proc. Imp. Acad. Tokyo*, 1932, **8**, 119), from 1 : 2 : 3 : 3-tetramethylindoleninium iodide, quinaldine methiodide, etc., indicate that such an intermediate condensation does not occur with the phthalazinium salt, although it forms the carbocyanine dye (VI) readily. Under parallel conditions 1 : 3 : 3-*trimethyl*-2-β-*acetanilido*- and -*anilino-vinylindoleninium perchlorates* are obtained with ease.

Mills and Braunholtz (J., 1922, **121**, 1489), and later Ogata (*loc. cit.*), demonstrated that the various classes of cyanine dyes exhibit a type of virtual tautomerism involving the transference of the acid radical from one of the two nitrogen atoms to the other, by obtaining identical products from two processes which, in the absence of such an intramolecular change, should have given isomerides differing in the nitrogen atoms to which the acid radical was attached. Mills and Braunholtz also pointed out that, although it was not determined which of the two possible formulæ should be assigned to the crystalline product, it will evidently be the salt derived from the stronger of the two corresponding bases. When a mixture of the perchlorate of (III; R = 4′-nitrophenyl), 1 : 3 : 3-trimethyl-2-methyleneindoline and diphenylformamidine, or ethyl orthoformate, is heated in acetic anhydride solution, a substance (A) is obtained as dark lustrous crystals, m. p. 246—250°, and the analytical results only approximate to those required by the desired indoleninophthalazinocyanine. On the other hand, 1 : 3 : 3-trimethyl-2-β-acetanilidovinylindoleninium perchlorate condenses with (III; R = 4′-nitrophenyl) in boiling acetic anhydride solution and (1 : 3 : 3-*trimethyl*-2-*indolenino*)(1′-*methoxy*-3′-p-*nitrophenyl*-3′ : 4′-*dihydro*-4′-*phthalazino*)-*carbocyanine perchlorate* (VII), m. p. 265° (decomp.), is obtained. This method also gives the 2″ : 6″-*dichloro*-4″-*nitro*-analogue, but the crude *m*-nitrophenyl isomeride was isolated only as a resin soluble in methyl alcohol with a violet-blue colour. As a result of a difficult fractional crystallisation from acetic anhydride, the substance (A) above was found to be a mixture of (VI; R = 4″-nitrophenyl) and (VII). This appears to support the view that the positive charge is more under the influence of one nitrogen atom than the other. Consequently, an unsymmetrical compound will be obtained in good yield only when the reaction is carried out with, as salt, that compound the nitrogen atom of which in the product bears the positive charge, and, as base, that compound the nitrogen atom of which in the product is tertiary. Otherwise double decomposition must occur and so, in the presence of ethyl orthoformate or diphenylformamidine, render possible the production of two symmetrical dyes, in addition to the unsymmetrical one. Although in the present case, we isolated only the latter (VII) and one of the former (VI), the presence of the much more soluble bis-(1 : 3 : 3-trimethyl-2-indolenino)carbocyanine perchlorate was indicated by the violet colour of the filtrate from substance (A). This view is supported by the results of Ogata (*loc. cit.*), for, although he isolated identical products from his two processes, in all cases that he examined the yield from one method was twice that from the other.

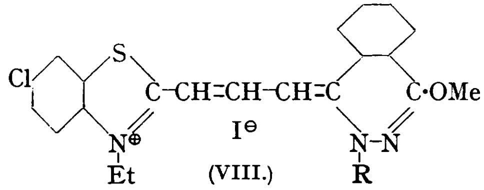

(VI.)

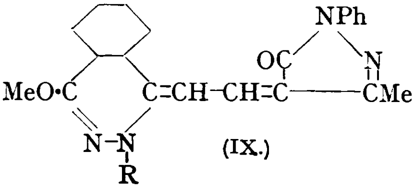

(VII.)

The perchlorates (VII) are not very soluble and it was thought that an unsymmetrical polymethin dye might be isolated as a more soluble iodide if a very reactive highly basic compound was used as first component with (III) as second component, despite the low reactivity of the latter. Consequently, 5-chloro-2-β-acetanilidovinylbenzthiazole ethiodide, prepared from 5-chloro-1-methylbenzthiazole ethiodide and diphenylformamidine, was condensed with (III; R = 2′ : 6′-dichloro-4′-nitrophenyl), and (5-*chloro*-2-*ethyl*-1-*benzthiazolo*)(1′-*methoxy*-3′-[2″ : 6″-*dichloro*-4″-*nitrophenyl*]-3′ : 4′-*dihydro*-4′-*phthalazino*)*carbocyanine iodide* (VIII) obtained; it was moderately soluble in methyl alcohol.

Attempts to prepare penta- and hepta-methin (di- and tri-carbocyanine) dyes containing a phthalazine residue or residues by the methods of Beattie, Heilbron, and Irving (J., 1932, 260) and Fisher and Hamer (J., 1933, 189), respectively, were unsuccessful.

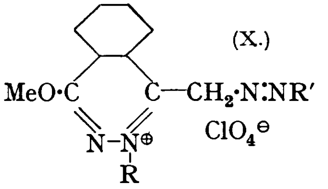
Orange dyes have been prepared by condensing 1-phenyl-3-methyl-4-anilinomethylene-5-pyrazolone with the ψ-base of quinaldine methiodide, 1 : 3 : 3-trimethyl-2-methylene-indoline, etc. (Imperial Chemical Industries Ltd., Rodd, and Watts, B.P. 366,964). Compound (III; R = 4′-nitrophenyl) condenses similarly with the pyrazolone with formation of 1-*methoxy*-3-p-*nitrophenyl*-4-(5′-*keto*-1′-*phenyl*-3′-*methylpyrazolinylidene-ethylidene*)-3 : 4-*dihydrophthalazine* (IX).


(VIII.)

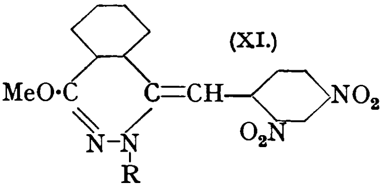

(IX.)

König (*Ber.*, 1923, **56**, 1543; 1924, **57**, 144, 891; cf. Adam, *Wissensch. Ind.*, 1923, **2**, 2; Humphries, J., 1926, 374) studied the coupling of diazotised aniline or *p*-nitroaniline with quinaldine, benzthiazole and indoline ψ-bases and found that, although various complications can occur, with a suitable technique the *N*-alkyl group is not eliminated and somewhat unstable azo-dye bases, which form stable salts with strong acids, are produced. Compounds (III; R = 4′-nitrophenyl, 2′ : 6′-dichloro-4′-nitrophenyl, or 3′-nitrophenyl) couple readily with diazotised aniline or *p*-nitroaniline under carefully controlled conditions of acidity and in absence of excess nitrous acid, and the resulting azo-compounds are isolated as their stable *perchlorates* (X; R′ = phenyl or 4″-nitrophenyl). Azo-compounds of this type exhibit halochromism. The benzeneazomethyl compounds are deeper coloured (red) in solution than the corresponding *p*-nitro-analogues (orange), and when alkali is added to the solutions, the former are little altered, whereas the latter are coloured violet and a violet precipitate separates. Diazotised *p*-aminobenzoic, anthranilic, sulphanilic, and 1-amino-8-naphthol-3 : 6-disulphonic acids also were coupled with (III); the products separated from the reaction mixtures and appeared to be internal salts of the respective monoazo-compounds, but they were not obtained pure.

(X.)



(XI.)



Experiments such as those of Humphries (*loc. cit.*) with *p*-nitrophenylnitrosoamine and cold alcoholic solutions of quaternary salts could not be carried out with the phthalazinium salts owing to the insolubility of the latter under these conditions. The only evidence that the perchlorates of (III) react with phenylhydrazine in the manner described by Rosenhauer (*Ber.*, 1924, **57**, 1192) for 1 : 2 : 3 : 3-tetramethylindoleninium iodide was the production of deep red colours.

Attempts to prepare addition products of (III) with carbon disulphide (cf. Schneider, Gaertner, and Jordan, *Ber.*, 1924, **57**, 522; König, *ibid.*, 1928, **61**, 2069), or reaction products of the perchlorates of (III) with 4 : 4′-bisdimethylaminobenzhydrol (cf. Humphries, *loc. cit.*), were unsuccessful.

Although it is well known that primary and secondary arylamines and pyridine react with 2 : 4-dinitrochlorobenzene to form *N*-dinitrophenyl derivatives, the reaction of this reagent with bases containing external methylene groups does not appear to have been recorded hitherto. Compounds (III; R = 4′- or 3′-nitrophenyl) readily condense with 2 : 4-dinitrochlorobenzene in boiling alcoholic solution with elimination of hydrogen chloride (the yield is doubled in presence of potassium acetate) and formation of 1-*methoxy*-3-(4′- and 3′-*nitrophenyl*)-4-(2″ : 4″-*dinitrobenzylidene*)-3 : 4-*dihydrophthalazine* (XI). Similarly 1 : 3 : 3-trimethyl-2-methyleneindoline and the ψ-base of quinaldine ethiodide yield respectively 2-(2′ : 4′-*dinitrobenzylidene*)-1 : 3 : 3-*trimethylindoline* and 2-(2′ : 4′-*dinitrophenyl*)-1-*ethyl*-1 : 2-*dihydroquinoline*. The ψ-base of α-picoline ethiodide also reacted readily, but the product was isolated only as a resin, soluble in alcohol with a deep pure blue colour and soluble in concentrated sulphuric acid to a colourless solution, changing to intense blue on dilution. This indicates low basicity and, in conjunction with its much deeper colour than that of derivatives of more complex heterocyclic systems, suggests that condensation with 2 molecules of 2 : 4-dinitrochlorobenzene may have occurred in this case.

Even acetoacetic ester and malonic ester appear to react with 2 : 4-dinitrochlorobenzene in boiling alcoholic solution in presence of potassium acetate, in that potassium chloride is deposited and deep red and yellow colours respectively are developed, but no solid products could be isolated in either case. 1-Phenyl-3-methyl-5-pyrazolone, however, gives the 4-(2′ : 4′-*dinitrophenyl*) derivative.

The optical sensitising properties of the compounds described when added to silver halide emulsions have been kindly tested in the Research Laboratories of Kodak Ltd. None has any marked sensitising properties, but all, except (IX; R = 4′-nitrophenyl), function as desensitisers in varying degrees: (V; R = 4′-nitrophenyl or 2′ : 6′-dichloro-4′-nitrophenyl), (VI; R = 4″- or 3″-nitrophenyl), (VII; R = 4″-nitrophenyl or 2″ : 6″-dichloro-4″-nitrophenyl), and (VIII; R = 2″ : 6″-dichloro-4″-nitrophenyl) are all good desensitisers, but the remaining compounds are moderate to weak desensitisers.

Finally, 4′- and 3′-nitro-3-phenylphthalaz-1-one were methylated with improved results in the absence of nitrobenzene (cf. J., 1928, 2554, 2562), a somewhat higher temperature being necessary than with their 4-methyl homologues (I), and converted into their *perchlorates*, which are hydrolysed more easily than the perchlorates of (III). Neither 1-methoxy-3-(4′- or 3′-nitrophenyl)phthalazinium perchlorate nor the bases undergo any of the reactions reported in the present paper, and the activity of such bases appears to be limited to combination with alcohols and conversion into 4-keto-1-methoxy-3-nitroaryl 3 : 4-dihydrophthalazines by heat.

EXPERIMENTAL.

The preparation of 4′-nitro-3-phenyl-4-methylphthalaz-1-one from 1-hydroxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid as already described (J., 1931, 1070), but on a larger scale, gave an improved yield (69 g. from 100 g. of the nitro-acid; 80·3%).

3′-Nitro-3-phenyl-4-methylphthalaz-1-one (J., 1931, 1921) was prepared by a better method. A solution of chromium trioxide (7·5 g.) in glacial acetic acid (50 c.c.) and water (20 c.c.) was dropped into a solution of 1-hydroxy-3-(3′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid (20 g.) in glacial acetic acid (150 c.c.) at 20° during 2 hours with vigorous stirring. Next day (vol. then 110 c.c.), the light brown precipitate of the complex salt (15 g.) was collected, washed with a little acetic acid, and stirred with cold aqueous ammonia, and the almost colourless product filtered off and washed with water (yield, 9·1 g.); the filtrate contained ammonium chromate. A further quantity (3·6 g.) was isolated by adding much ice-water to the acetic acid filtrate and almost neutralising it with aqueous ammonia below 30° (total yield, 73·9%). 3′-Nitro-3-phenyl-4-methylphthalaz-1-one crystallised best from dry methyl alcohol in small, pale yellow prisms, m. p. 260° (decomp.) (not 249° as previously given) after becoming colourless at about 70°.

Action of Methyl Sulphate.—The 1-methoxy-3-(nitroaryl)-4-methylene-3 : 4-dihydrophthalazines were prepared by the following improved procedure. 4′-Nitro-3-phenyl-4-methylphthalaz-1-one (25 g.) and methyl sulphate (20 g.) were stirred at 50° for 20 minutes. The viscous mixture was poured into boiling water (300 c.c.), left over-night, and filtered. The filtrate was almost neutralised, boiled (charcoal), and filtered, the filtrate left over-night, and slightly basic impurities filtered off. The filtrate, rendered alkaline with sodium carbonate, gave an orange-yellow gelatinous precipitate (probably the ammonium hydroxide II), which coagulated almost immediately to a red solid (the ψ-base III), and this crystallised from ethyl acetate in orange-red needles, m. p. 134° (yield, 20·5 g.; 78·1%). The ψ-base is readily soluble in dilute acids and its less soluble salts are precipitated from a concentrated hydrochloric acid solution. Such salts, except the perchlorate, are unstable and cannot be crystallised or purified. 20% Perchloric acid (40 c.c.) was added to the aqueous solution of the methosulphate prepared as described above; the precipitated 1-*methoxy*-3-(4′-*nitrophenyl*)-4-*methylphthalazinium perchlorate* crystallised from 50% acetic acid containing perchloric acid in almost colourless, flat prisms, m. p. 199° (decomp.) after softening and reddening (yield, 28 g.; 79·6%) (Found : C, 48·6; H, 3·5; N, 10·7. $C_{16}H_{14}O_3N_3,ClO_4$ requires C, 48·55; H, 3·5; N, 10·6%).

In the case of the 2′ : 6′-dichloro-4′-nitro-analogue, the methylation mixture was heated at 60—70° for 3 hours. The red ψ-base crystallised from ethyl acetate in large, brownish-red, rectangular prisms, m. p. 136° (yield, 20·8 g.; 80%). 1-*Methoxy*-3-(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-4-*methylphthalazinium perchlorate* crystallised from 50% acetic acid containing perchloric acid in almost colourless, prismatic needles, m. p. 228° (yield, 25 g.; 75·4%) (Found : N, 9·0; Cl, 22·4. $C_{16}H_{12}O_3N_3Cl_2,ClO_4$ requires N, 9·05; Cl, 22·9%).

In the case of the 3′-nitro-analogue, an orange-yellow precipitate was obtained and this coagulated suddenly to the dark reddish-brown resinous ψ-base, which could not be crystallised, but was washed with water and dried in a desiccator (yield, 16 g.). 1-*Methoxy*-3-(3′-*nitrophenyl*)-4-*methylphthalazinium perchlorate* crystallised from 50% acetic acid in colourless plates, m. p. 223—224° (yield, 19 g.; 54%) (Found : C, 48·5; H, 3·7; N, 10·5; Cl, 8·8. $C_{16}H_{14}O_3N_3,ClO_4$ requires C, 48·55; H, 3·5; N, 10·6; Cl, 9·0%).

1-*Methoxy*-3-(4′- *and* 3′-*nitrophenyl*)*phthalazinium Perchlorates.*—4′- or 3′-Nitro-3-phenylphthalaz-1-one (3 g.) and methyl sulphate (5 g.) were kept at 90° for 1 hour (cf. J., 1928, 2554, 2562). The viscous brown solution was poured into boiling water (50 c.c.), boiled for 5 minutes, water (150 c.c.) added, and the whole left over-night. After filtration, the filtrate was treated with 20% perchloric acid (20 c.c.). 1-*Methoxy*-3-(4′-*nitrophenyl*)*phthalazinium perchlorate* crystallised from aqueous acetic acid containing perchloric acid in almost colourless, long needles, which changed to prisms, m. p. 249° (yield, 3·9 g.; 96·1%) (Found : C, 47·4; H, 3·35; N, 11·0. $C_{15}H_{12}O_3N_3,ClO_4$ requires C, 47·2; H, 3·15; N, 11·0%), and the 3′-*nitro*-isomeride in colourless, long, prismatic needles, m. p. 215° (yield, 4 g.; 98·5%) (Found : C, 47·1; H, 3·2; N, 11·1%).

Action of Nitrous Acid or p-*Nitrosodimethylaniline on* 1-*Methoxy*-3-(4′-*nitrophenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine.*—(a) A solution of sodium nitrite (1 g.) in water (2 c.c.) was dropped into a solution of the methylene base (3 g.) in glacial acetic acid (20 c.c.) at 0° during 1 hour. A white precipitate separated progressively and hydrogen cyanide was evolved. After keeping for a further hour at 0°, the mixture was left over-night at room temperature, and the precipitate then collected. The product was 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine, m. p. and mixed m. p. 199° (yield, 2·5 g.; 82·8%), confirmed by conversion into 1 : 4-diketo-3-(4′-nitrophenyl)tetrahydrophthalazine, m. p. and mixed m. p. 307° (cf. J., 1928, 2554; 1935, 1811). Addition of 20% perchloric acid (20 c.c.) 10 minutes after all the sodium nitrite solution had been added, however, precipitated 1-methoxy-3-(4′-nitrophenyl)-4-methylphthalazinium perchlorate (3·5 g.), indicating that the reaction is slow. (b) A solution of *p*-nitrosodimethylaniline (2 g.) in alcohol (75 c.c.) was added to a solution of the methylene base (4 g.) in hot alcohol (100 c.c.), and the mixture refluxed for 1 hour. After a few minutes, 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine separated progressively (yield, 2·5 g.; 62%).

Action of Benzyl Iodide on 1-*Methoxy*-3-(4′- *and* 3′-*nitrophenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine*.—A solution of benzyl iodide (9 g.; 1·35 mols.) in alcohol (15 c.c.) was added to a solution of the methylene base (9 g.) in boiling alcohol (75 c.c.). The red mixture was refluxed (3 hours for the 4′- and 1 hour for the 3′-nitro-compound), and the resulting greenish-yellow solution filtered hot. 1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(β-*phenylethyl*)*phthalazinium iodide* crystallised from ethyl alcohol in long yellow needles, m. p. 185° after softening at 175° (yield, 4·5 g.; 28·8%) (Found: C, 54·0; H, 4·0; N, 7·8; I, 24·95. $C_{23}H_{20}O_3N_3I$ requires C, 53·85; H, 3·9; N, 8·2; I, 24·7%); the 3′-*nitro*-isomeride crystallised from methyl alcohol–ethyl alcohol (1 : 4) in yellow prismatic needles, m. p. 174° after softening at 170° (yield, 13·6 g.; 87%) (Found: C, 53·7; H, 4·1; N, 8·0; I, 24·3%), readily soluble in methyl alcohol but only sparingly soluble in ethyl alcohol.

(1 : 3 : 3-*Trimethyl*-2-*indolenino*)(1′-*methoxy*-3′-p-*nitrophenyl*-3′ : 4′-*dihydro*-4′-*phthalazino*)-*cyanine Perchlorate* (IV).—1-Methoxy-3-(4′-nitrophenyl)-4-methylene-3 : 4-dihydrophthalazine (3 g.) was added to a solution of 2-oximinomethyl-3 : 3-dimethylindolenine methoperchlorate (3 g.) (Kuhn, Winterstein, and Balser, *Ber.*, 1930, **63**, 3182; the use of sodium nitrite in 200 c.c. of water as given by these authors for the preparation of this compound gave much tarry material, whereas the use of 20 c.c. of water gave the yield of 96% claimed) in acetic anhydride (15 c.c.). The temperature rose immediately, the colour of the solution became deep red, and hydrogen cyanide was evolved. After heating for 1 hour on a boiling water-bath, and addition of alcohol (15 c.c.), the solution was boiled and then cooled in a freezing mixture until the oil which separated had solidified. The *cyanine perchlorate* was washed with alcohol and ether and formed pale red plates, m. p. 182° with local melting at 178° (yield, 2·7 g.; 48%) (Found: N, 11·3. $C_{27}H_{25}O_3N_4,ClO_4$ requires N, 10·15%), which could not be recrystallised or purified further owing to the ease of hydrolysis.

1-*Methoxy*-3-(4′-*nitro*-, 2′ : 6′-*dichloro*-4′-*nitro*-, *and* 3′-*nitro-phenyl*)-4-p-*dimethylaminostyrylphthalazinium Perchlorate* (V).—*p*-Dimethylaminobenzaldehyde (2 g.) was added to a solution of the 1-methoxy-3-(nitroaryl)-4-methylphthalazinium perchlorate (3 g.) in glacial acetic acid (10 c.c.) and acetic anhydride (20 c.c.); the mixture was heated at 100° under reflux for 5 hours and left to crystallise.

1-*Methoxy*-3-(4′-*nitrophenyl*)-4-p-*dimethylaminostyrylphthalazinium perchlorate* dissolved in acetic anhydride with a deep purple colour and crystallised in fine, lustrous, dark green needles, m. p. 238° (yield, 3·5 g.; 87·6%) (Found: C, 57·1; H, 4·3; N, 10·5; Cl, 6·4. $C_{25}H_{23}O_3N_4,ClO_4$ requires C, 57·0; H, 4·4; N, 10·6; Cl, 6·7%); the 2′ : 6′-*dichloro*-4′-*nitro*-analogue separated from the reaction mixture in lustrous, dark green, prismatic needles, m. p. 254° (decomp.), which dissolved in acetic anhydride with a deep blue colour and crystallised in small, dark green prisms with a golden reflex, m. p. 254° (decomp.) (yield, 3 g.; 78%) (Found: C, 50·3; H, 3·6; N, 9·5; Cl, 17·5. $C_{25}H_{21}O_3N_4Cl_2,ClO_4$ requires C, 50·4; H, 3·5; N, 9·4; Cl, 17·9%), but otherwise both modifications possess identical properties; and the 3′-*nitro*-analogue dissolved in acetic anhydride with a deep purple colour, redder than that of the 4′-nitro-isomeride, and separated as a black amorphous powder, m. p. 198° (yield, 3·7 g.; 92·6%) (Found: C, 56·6; H, 4·3; N, 10·4%).

Bis-(1-*methoxy*-3-p- *and* -m-*nitrophenyl*-3 : 4-*dihydro*-4-*phthalazino*)*carbocyanine Perchlorates* (VI).—(a) Ethyl orthoformate (0·4 g.) was added to a solution of 1-methoxy-3-(4′-nitrophenyl)-4-methylphthalazinium perchlorate (1 g.) and the corresponding methylene base (0·75 g.) in acetic anhydride (6 c.c.). The solution was kept just below its b. p. for ½ hour, during which the colour changed through deep brown to deep bluish-green and crystals of the product separated (yield, 0·85 g.; 48%). (b) Diphenylformamidine (1·8 g.) was added to a solution of the methylphthalazinium perchlorate (3·7 g.) and the methylene base (2·8 g.) in acetic anhydride (15 c.c.), and the solution boiled intermittently for 5 minutes (yield, 5·3 g.; 80·8%).

*Bis-(1-methoxy-3-*p*-nitrophenyl-3 : 4-dihydro-4-phthalazino)carbocyanine perchlorate* crystallised from acetic anhydride in small dark prisms with a copper lustre, m. p. 258—260° (decomp.) (Found : C, 56·1; H, 3·7; N, 11·1; Cl, 4·9. $C_{33}H_{25}O_6N_6,ClO_4$ requires C, 56·5; H, 3·6; N, 12·0; Cl, 5·1%), insoluble in boiling water, very sparingly soluble in boiling acetic anhydride, and soluble in cold concentrated sulphuric acid, the colourless solution changing to bluish-green on dilution. It was converted by boiling dilute nitric acid into 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine.

The m-*nitro*-isomeride, prepared by method (b), on addition of methyl alcohol at intervals to the reaction mixture, was isolated as a tar which ultimately solidified and crystallised from methyl alcohol in minute dark prisms with a bronze lustre, m. p. 244° (decomp.) (yield, 4·5 g.; 70·2%) (Found : C, 56·7; H, 3·85; N, 12·1; Cl, 5·3%), much more soluble than the *p*-nitro-isomeride and giving solutions of a bluer shade of green.

1 : 3 : *3-Trimethyl-2-β-acetanilidovinylindoleninium Perchlorate* (cf. Imperial Chemical Industries Ltd., Piggott, and Rodd, B.P. 344,409).—Diphenylformamidine (7 g.) was added to a solution of 1 : 2 : 3 : 3-tetramethylindoleninium perchlorate (10 g.) in boiling acetic anhydride (34 c.c.), the mixture refluxed for 20 minutes, then cooled, and the crystals collected. 1 : 3 : 3-*Trimethyl-2-β-acetanilidovinylindoleninium perchlorate* crystallised from acetic anhydride in yellow needles, m. p. 245° (yield, 11 g.; 71·9%) (Found : C, 59·6; H, 5·8; N, 6·6; Cl, 8·5. $C_{21}H_{23}ON_2,ClO_4$ requires C, 60·2; H, 5·5; N, 6·7; Cl, 8·5%). The acetyl group is hydrolysed by boiling a glacial acetic acid solution with concentrated hydrochloric acid.

1 : 3 : *3-Trimethyl-2-β-anilinovinylindoleninium Perchlorate.*—An intimate mixture of diphenylformamidine (2 g.) and 1 : 2 : 3 : 3-tetramethylindoleninium perchlorate (3 g.) was heated at 150° for 5 minutes and then allowed to cool to 80° during 5 minutes. The resinous product was rendered crystalline and most of the red colour removed by boiling with alcohol (20 c.c.). 1 : 3 : *3-Trimethyl-2-β-anilinovinylindoleninium perchlorate* crystallised from methyl alcohol in long, orange-yellow, prismatic needles with a purple reflex, m. p. 253° (yield, 2·4 g.; 58·1%) (Found : C, 60·0; H, 5·6; N, 7·6. $C_{19}H_{21}N_2,ClO_4$ requires C, 60·5; H, 5·6; N, 7·4%), converted by acetic anhydride into the preceding acetyl derivative.

(1 : 3 : *3-Trimethyl-2-indolenino)(1′-methoxy-3′-[4″-nitro- and 2″ : 6″-dichloro-4″-nitrophenyl]-3′ : 4′-dihydro-4′-phthalazino)carbocyanine Perchlorate* (VII).—1-Methoxy-3-(4′-nitrophenyl)-4-methylene-3 : 4-dihydrophthalazine (1·5 g.) was added to a solution of 1 : 3 : 3-trimethyl-2-β-acetanilidovinylindoleninium perchlorate (2 g.) in boiling acetic anhydride (25 c.c.), the mixture boiled for 6 minutes, and the deep blue solution left to crystallise. The *carbocyanine perchlorate* crystallised from acetic anhydride in aggregated green prisms with a golden lustre, m. p. 265° (decomp.) (yield, 2·5 g.; 85%) (Found : C, 59·8; H, 4·9; N, 9·5; Cl, 6·1. $C_{29}H_{27}O_3N_4,ClO_4$ requires C, 60·15; H, 4·7; N, 9·7; Cl, 6·1%).

The 2″ : *6″-dichloro-4″-nitro*-analogue, prepared similarly, except that ether was added to the deep bluish-violet reaction mixture to induce crystallisation, separated from acetic anhydride in aggregated small green prisms with a golden lustre, m. p. 246° with preliminary softening (yield, 72%) (Found : N, 8·85; Cl, 16·0. $C_{29}H_{25}O_3N_4Cl_2,ClO_4$ requires N, 8·65; Cl, 16·45%).

(5-Chloro-2-ethyl-1-benzthiazolo)(1′-methoxy-3′-[2″ : 6″-dichloro-4″-nitrophenyl]-3′ : 4′-dihydro-4′-phthalazino)carbocyanine Iodide (VIII).—Finely powdered 5-chloro-2-β-acetanilidovinylbenzthiazole ethiodide (0·4 g.), m. p. 249° (decomp.), prepared from 5-chloro-1-methylbenzthiazole ethiodide (cf. König, *Ber.*, 1928, **61**, 2069; Beilenson and Hamer, this vol., p. 1228) and diphenylformamidine, was extracted (Soxhlet) during 15 minutes with boiling acetic anhydride (10 c.c.), in which 1-methoxy-3-(2′ : 6′-dichloro-4′-nitrophenyl)-4-methylene-3 : 4-dihydrophthalazine (0·4 g.) was dissolved, and the solution left to crystallise. The *carbocyanine iodide* (VIII) crystallised from acetic anhydride in dark brown plates with a dull green lustre, m. p. 254° (yield, 0·45 g.; 57·4%) (Found : C, 45·5; H, 3·1; 4·531 mg. gave 4·160 mg. AgCl + AgI. $C_{27}H_{20}O_3N_4SCl_3,I$ requires C, 45·4; H, 2·8%; AgCl + AgI, 4·226 mg.), moderately easily soluble in methyl alcohol with a bluish-violet colour.

*1-Methoxy-3-*p*-nitrophenyl-4-(5′-keto-1′-phenyl-3′-methylpyrazolinylidene-ethylidene)-3 : 4-dihydrophthalazine* (IX).—A solution of 1-methoxy-3-(4′-nitrophenyl)-4-methylene-3 : 4-dihydrophthalazine (3 g.) and 1-phenyl-3-methyl-4-anilinomethylene-5-pyrazolone (3 g.) (cf. Dains and Brown, *J. Amer. Chem. Soc.*, 1909, **31**, 1154) in acetic anhydride (10 c.c.) and glacial acetic acid (16 c.c.) was heated at 100° for 6 hours, and the crystalline *product* (IX) collected next day. It crystallised from acetic anhydride in small black prisms with a green lustre, m. p. 258° (yield, 2 g.; 41%) (Found : C, 67·7; H, 4·5; N, 14·5. $C_{27}H_{21}O_4N_5$ requires C, 67·6; H, 4·4; N, 14·6%), sparingly soluble in most organic solvents with a bluish-violet colour, and soluble in concentrated sulphuric acid with a greenish-yellow colour, changing to yellow on dilution. The perchlorate crystallised from 50% acetic acid in small yellow prisms of indefinite m. p.

Azo-derivatives of 1-*Methoxy*-3-(4′-*nitro*-, 2′ : 6′-*dichloro*-4′-*nitro*-, *and* 3′-*nitro-phenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine* (X).—1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(*benzeneazomethyl*)*phthalazinium perchlorate.* Aniline (1 g.) in glacial acetic acid (15 c.c.) and concentrated hydrochloric acid (5 c.c.) was diazotised at 0° (sodium nitrite 0·8 g., water 2 c.c.) and after 15 minutes the excess of nitrous acid was destroyed and mineral acid replaced by the addition of urea and sodium acetate respectively. The filtered diazo-solution was added to a solution of the methylene base (3 g.) in acetic acid (10 c.c.) and kept at 0° for 1 hour and then at room temperature for 1 hour. 20% Perchloric acid (75 c.c.) was finally added to the deep red solution with vigorous stirring, and the precipitated perchlorate collected. 1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(*benzeneazomethyl*)*phthalazinium perchlorate* crystallised from methyl alcohol–acetic acid (1 : 3) in long, reddish-brown, prismatic needles, m. p. 224° (yield, 5 g.; 98·4%) (Found : C, 53·0; H, 3·8; N, 13·4; Cl, 6·85. $C_{22}H_{18}O_3N_5,ClO_4$ requires C, 52·85; H, 3·6; N, 14·0; Cl, 7·1%), soluble in cold concentrated sulphuric acid with an intense bluish-violet colour, changing to orange-brown on dilution.

The 3′-nitro-isomeride was a red amorphous powder of indefinite m. p., soluble in concentrated sulphuric acid with an intense pure blue colour, changing to orange on dilution.

1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(4″-*nitrobenzeneazomethyl*)*phthalazinium perchlorate,* prepared similarly from diazotised *p*-nitroaniline, crystallised from 70% acetic acid in red prisms with a bluish lustre, m. p. 268° (yield, 5·5 g.; 99·3%) (Found : C, 48·6; H, 3·2; N, 14·8; Cl, 6·3. $C_{22}H_{17}O_5N_6,ClO_4$ requires C, 48·5; H, 3·1; N, 15·4; Cl, 6·5%), soluble in concentrated sulphuric acid with an orange-red colour, changing to orange-yellow on dilution. A violet precipitate was obtained when an acid solution was rendered alkaline, and the following two azo-compounds behaved similarly.

The 3′-*nitro*-isomeride, after repeated treatment with acetone, formed a red semi-crystalline powder, m. p. 235° (yield, 4·4 g.; 79·5%) (Found : C, 47·9; H, 3·4%), soluble in concentrated sulphuric acid with an orange-red colour, changing to orange on dilution.

1-*Methoxy*-3-(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-4-(4″-*nitrobenzeneazomethyl*)*phthalazinium perchlorate.* When the above conditions of diazotisation and coupling were used, the product separated directly from the mixture and was probably the chloride of the azo-dye base, which is readily hydrolysed. Consequently, hydrochloric acid was omitted. A solution of *p*-nitroaniline (1·1 g.) in warm acetic acid (10 c.c.) was poured on ice (10 g.) and acetic acid (5 c.c.); diazotisation, coupling, and isolation of the perchlorate were then carried out under similar conditions to those described above. The *phthalazinium perchlorate* crystallised from 70% acetic acid containing perchloric acid in lustrous orange-yellow prisms, m. p. 254° (yield, 4·5 g.; 89%) (Found : C, 42·9; H, 2·85; N, 13·8. $C_{22}H_{15}O_5N_6Cl_2,ClO_4$ requires C, 43·0; H, 2·4; N, 13·7%), soluble in concentrated sulphuric acid with an orange-red colour, changing to orange on dilution.

Action of 2 : 4-*Dinitrochlorobenzene on* 1-*Methoxy*-3-(4′- *and* 3′-*nitrophenyl*)-4-*methylene*-3 : 4-*dihydrophthalazine, etc.*—1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(2″ : 4″-*dinitrobenzylidene*)-3 : 4-*dihydrophthalazine* (XI). 2 : 4-Dinitrochlorobenzene (2 g.) was added to a boiling solution of the methylene base (2 g.) in alcohol (100 c.c.), followed by potassium acetate (3 g.), and the mixture refluxed (½ hour for the 4′- and 4 hours for the 3′-nitro-compound). A deep red colour developed rapidly and the product separated progressively. 1-*Methoxy*-3-(4′-*nitrophenyl*)-4-(2″ : 4″-*dinitrobenzylidene*)-3 : 4-*dihydrophthalazine* crystallised from acetic anhydride in minute black prisms with a bronze reflex, m. p. 255° (yield, 2·9 g.; 92·8%) (Found : C, 57·2; H, 3·4; N, 15·2. $C_{22}H_{15}O_7N_5$ requires C, 57·3; H, 3·25; N, 15·2%), sparingly soluble in alcohol and benzene with a reddish-brown colour, and soluble in concentrated mineral acids with a pale yellow colour, unchanged on dilution, but a reddish-brown flocculent precipitate separated when the acid solution was rendered alkaline.

The 3′-*nitro*-isomeride, soluble in organic solvents with a cherry-red colour, crystallised from alcohol in minute black prisms with a bronze reflex, m. p. 210° (yield, 2·4 g.; 76·8%) (Found : C, 57·2; H, 3·4; N, 15·5%), which reddened rapidly on exposure to light owing to surface decomposition.

2-(2′ : 4′-*Dinitrobenzylidene*)-1 : 3 : 3-*trimethylindoline,* prepared from 1 : 3 : 3-trimethyl-2-methyleneindoline (5 g.) under similar conditions, but refluxed for 6 hours, after which unaltered base was still present, crystallised from alcohol in black prisms with a green lustre, or large rhombs, m. p. 137° (yield, 4 g.; 40·8%) (Found: C, 63·9; H, 5·1; N, 12·3. $C_{18}H_{17}O_4N_3$ requires C, 63·7; H, 5·0; N, 12·4%).

2-(2′ : 4′-*Dinitrobenzylidene*)-1-*ethyl*-1 : 2-*dihydroquinoline*, prepared from quinaldine ethiodide (2 g.) under similar conditions, but refluxed for 3 hours, after purification with benzene, crystallised from alcohol in fine black needles with a green lustre, m. p. 180° (yield, 0·5 g.; 22·2%) (Found: C, 64·4; H, 4·6; N, 13·0. $C_{18}H_{15}O_4N_3$ requires C, 64·1; H, 4·45; N, 12·5%), sparingly soluble in alcohol with a violet colour.

1-*Phenyl*-4-(2′ : 4′-*dinitrophenyl*)-3-*methyl*-5-*pyrazolone*, prepared from 1-phenyl-3-methyl-5-pyrazolone (3 g.) under similar conditions, but refluxed for 2 hours, was precipitated with water; the crude product (6·1 g.), after repeated crystallisation from methyl alcohol, formed small, golden-yellow, hexagonal plates, m. p. 215° (Found: C, 56·2; H, 3·9; N, 16·3. $C_{16}H_{12}O_5N_4$ requires C, 56·45; H, 3·5; N, 16·5%), soluble in dilute sodium hydroxide solution with an orange-brown colour and reprecipitated by acids.

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