

6. *Chemiluminescent Organic Compounds. Part III.*
*N-Methylated Phthalaz-1 : 4-diones.**

By H. D. K. DREW, H. H. HATT, and F. A. HOBART.

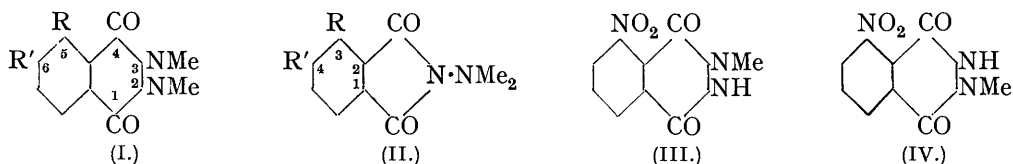
PHthalaz-1 : 4-DIONES show luminescence only when oxidised in solutions containing alkali, and therefore preliminary enolisation (lactim formation) has been assumed to occur. We wished to examine this hypothesis by finding what effect on the luminescence, particularly of the highly luminescent amino-derivatives, took place when one or both of the enolisable hydrogen atoms were replaced by the immobile methyl group. Direct methylation of the diones might give methylated lactim or lactam forms or a mixture of both; and therefore the methylated compounds were prepared by acting upon phthalic anhydrides and phthalimides with methylated hydrazines, whereby only *N*-methyl derivatives can result.

Rowe and Peters (J., 1933, 1331) prepared 2-methylphthalaz-1 : 4-dione from phthalic anhydride and methylhydrazine in acetic acid. We have not been able to prepare the 5-ring isomeride, *N*-methylaminophthalimide, either by modifying this reaction or by the action of methylhydrazine on phthalimide. It appears, therefore, that 6-ring formation is

* Since the completion of this paper a memoir by Zellner and Dougherty (*J. Amer. Chem. Soc.*, 1936, **58**, 1811) has appeared which covers common ground. Their descriptions of substances differ markedly from ours in a number of instances.

enhanced by the presence of the methyl group in the open-chain intermediate compounds (compare the case of hydrazine, Part I, this vol., p. 16); this conclusion receives some support from the fact that only the diones were isolated (see below) on condensing methylhydrazine with 3- or with 4-nitrophthalic anhydride.

Condensation of phthalic anhydride with *s*-dimethylhydrazine gave the colourless 2 : 3-*dimethylphthalaz-1 : 4-dione* (I; R = R' = H), as would be expected, and with *as*-dimethylhydrazine the more fusible, pale yellow isomeride, *N*-dimethylaminophthalimide



(II; R = R' = H). In a similar way, 5- and 6-nitro-2 : 3-dimethylphthalaz-1 : 4-diones and 3- and 4-nitro-*N*-dimethylaminophthalimides were obtained from 3- and 4-nitrophthalic anhydrides. By reduction of the nitro-compounds, 5- and 6-amino-2 : 3-dimethylphthalaz-1 : 4-diones were obtained.

As was to be anticipated, the action of methylhydrazine on 3-nitrophthalic anhydride gave a mixture separable into two isomerides, α - and β -5-nitro-*N*-methylphthalaz-1 : 4-diones, which behave as typical diones and so must comprise structures (III) and (IV); they are pale yellow substances forming colourless *acetyl* derivatives. The α -compounds are the less fusible and soluble, but it has not yet been ascertained whether they have the methyl group in the 2- or the 3-position. These nitro-compounds were reduced to the desired α - and β -5-amino-*N*-methylphthalaz-1 : 4-diones, the α - being the less fusible.

Parallel results were obtained in the condensation of 4-nitrophthalic anhydride with methylhydrazine; of the α - and β -6-nitro-*N*-methylphthalaz-1 : 4-diones, which are fairly readily separable, the α -form is the less soluble and fusible, and the same applies to the *acetyl* derivatives, but on the other hand β -6-amino-*N*-methylphthalaz-1 : 4-dione is less soluble and fusible than its α -isomeride.

A monomethyl derivative (m. p. 264°) of 5-nitrophthalaz-1 : 4-dione was obtained by Mihailescu and Protopopescu (*Bul. Soc. Chim. România*, 1930, **12**, 95) by the action of methyl sulphate; and a similar 6-nitro-compound (m. p. 298°) was prepared by Hoesch and Curtius (*J. pr. Chem.*, 1907, **76**, 301), using the same method. The descriptions are not sufficient to show whether these substances are identical with any of the four isomerides now described.

The 5-ring compounds and the dimethylated diones here described were devoid of luminescence; so also were the monomethylated 5- and 6-nitro-diones, but, of the four amino-derivatives prepared from them, three showed distinct though very feeble luminescence. The α -6-amino-compound did not glow on oxidation; of the remainder, the β -5-amino-compound was the most luminescent. The glows exhibited by these substances were all exceedingly feeble compared with that of the unmethylated 5-amino-dione, and therefore we cannot yet conclude that their luminescence is intrinsic and not the result of impurity;* further work is being carried out on the point. The present conclusion, therefore, is that the substitution of immobile groups for two of the enolisable hydrogen atoms of phthalaz-1 : 4-diones removes the luminescence, and that the substitution even for one of them very greatly diminishes, if it does not entirely remove, that property.

EXPERIMENTAL.

2-Methylphthalaz-1 : 4-dione, prepared by the method of Rowe and Peters (*loc. cit.*), formed colourless rhombic crystals (from glacial acetic acid), m. p. 238°. It also resulted in attempts to prepare *N*-methylaminophthalimide by the condensation of phthalimide and methylhydrazine under various conditions.

2 : 3-Dimethylphthalaz-1 : 4-dione.—Phthalic anhydride (5 g.), *s*-dimethylhydrazine dihydro-

* The presence of traces of hydrazine in the methyl- and dimethyl-hydrazine used would give rise to 5- and 6-aminophthalaz-1 : 4-diones, both of which are luminescent.

chloride (4.9 g.), and hydrated sodium acetate (10 g.) were refluxed together (3 hours) in 50% aqueous acetic acid; the acetic acid was then removed by repeated vacuum distillation with water. The residue crystallised from water in long, colourless, efflorescent needles of the *dihydrate* (Found, by detailed observation of the rate of loss of water at 20°: H₂O, 15.9. C₁₀H₁₀O₂N₂·2H₂O requires H₂O, 15.95%). The *anhydrous* substance, m. p. 175—176°, was white [Found: C, 63.3; H, 5.6; N, 14.7; *M* (in camphor), 188. C₁₀H₁₀O₂N₂ requires C, 63.15; H, 5.25; N, 14.75%; *M*, 190]. Hydrolysis by hot 2*N*-hydrochloric acid (3 hours) gave phthalic acid and dimethylhydrazine; boiling aqueous hydrazine gave the latter and phthalaz-1 : 4-dione.

N-Dimethylaminophthalimide.—Phthalic anhydride (2.4 g.) and *as*-dimethylhydrazine (1.0 g.) were heated together on the water-bath (2 hours); the oily red-brown product was boiled with water, the solution, on cooling, giving the required *substance* (1.4 g.), which crystallised from water (charcoal) in pale yellow plates, m. p. 125—126° [Found: C, 63.25; H, 5.35; *M* (in camphor), 185. C₁₀H₁₀O₂N₂ requires C, 63.15; H, 5.25%; *M*, 190], very soluble in alcohol or acetic acid. *N*-Hydrochloric acid hydrolysed it readily, producing phthalic acid, and treatment with hydrazine gave phthalaz-1 : 4-dione. The above condensation proceeded less favourably in acetic acid as solvent.

α - and β -5-Nitro-*N*-methylphthalaz-1 : 4-diones.—3-Nitrophthalic anhydride (2 g.), dissolved in glacial acetic acid (12 c.c.), was mixed slowly with methylhydrazine (1 g.), and the solution gently boiled under reflux (2 hours). The mixture, m. p. 235—245°, of two isomerides (1.9 g.) obtained on standing was separated either by taking advantage of the supersaturation of the β -isomeride in glacial acetic acid, or by acetylating the mixture (acetic anhydride) and fractionally crystallising the product from acetic acid; the pure α -acetyl derivative separated first and long needles of the β -acetyl derivative were slowly deposited from the mother-liquor after dilution with water. The acetyl derivatives were easily converted into the required nitro-compounds by shaking with dilute sodium hydroxide solution and precipitation with acid. The separations were followed by observing the m. p.'s and mixed m. p.'s of the several fractions. The α -nitro-compound formed very pale yellow, rhombic plates, m. p. 292° (decomp.) (Found: C, 49.1; H, 3.0; N, 19.6. C₉H₇O₄N₃ requires C, 48.85; H, 3.15; N, 19.0%), its sodium salt orange needles, and its *acetyl* derivative colourless rectangular or hexagonal prisms (from acetic acid) or long colourless needles (from alcohol), m. p. 204—205° (Found: C, 50.25; H, 3.4. C₁₁H₉O₅N₃ requires C, 50.2; H, 3.4%). The β -nitro-compound formed very pale yellow, pointed plates, m. p. 272° (decomp.) (Found: C, 49.15, 48.95; H, 3.35, 3.8; N, 19.3%); its *acetyl* derivative formed long, thin, colourless, pointed needles of tough texture, m. p. 158° (Found: C, 50.2; H, 3.7%); it is very triboelectric. Mixtures of the α - and the β -nitro-compound show a large depression of m. p.; and the same is true of their acetyl derivatives.

α - and β -5-Amino-*N*-methylphthalaz-1 : 4-diones.—These amines were obtained by reducing the above nitro-compounds with tin and concentrated hydrochloric acid at 30—40° with shaking. If they did not separate as stannichlorides from the filtered liquor, the whole was diluted with water and neutralised with excess of chalk, the mixture boiled and filtered, and the filtrate cautiously neutralised with dilute hydrochloric acid; the amine separated on standing. Tin can also be removed by hydrogen sulphide from solutions made just acid with acetic acid. The α -amine formed cream-coloured hexagonal columns from acetic acid, m. p. 308° (decomp.; sintering above 300°); dilute solutions had a blue fluorescence when cold (Found: C, 56.4; H, 5.0. C₉H₉O₂N₃ requires C, 56.55; H, 4.7%). The β -amine formed pale cream-coloured, long, thin needles from water, in which it was appreciably soluble; it melted at 299° (decomp.; superficial darkening from 240°) and depressed the m. p. of the α -isomeride; its solutions had a strong blue fluorescence (Found: C, 56.35; H, 5.2%). These amines dissolved at once in aqueous ammonia to colourless solutions; they were also soluble in mineral acids, to solutions which could be diazotised and coupled with alkaline β -naphthol, giving red alkali-soluble *azo*-compounds.

5-Nitro-2 : 3-dimethylphthalaz-1 : 4-dione.—A mixture of 3-nitrophthalic anhydride (7 g.), *s*-dimethylhydrazine hydrochloride (6 g.), anhydrous sodium acetate (6 g.), and acetic acid (35 c.c.) was heated under reflux (3 hours); the acetic acid was removed by repeated evaporation with water, and the residue washed with water, being then almost pure (6.8 g.). The *substance* crystallised from water in pale canary-yellow, anhydrous, rhombic platelets, m. p. 194—195° [Found: C, 50.95; H, 4.05; N, 18.3; *M* (in camphor), 241. C₁₀H₉O₄N₃ requires C, 51.05; H, 3.85; N, 17.85%; *M*, 235], very soluble in acetic acid but rather sparingly soluble in water or alcohol. Hydrolysis to *s*-dimethylhydrazine by hot 2*N*-hydrochloric acid required about 16 hours.

3-Nitro-*N*-dimethylaminophthalimide.—3-Nitrophthalic anhydride (3.1 g.) and *as*-dimethyl-

hydrazine (1 g.) were separately dissolved in a little acetic acid, and the solutions mixed; the acetic acid was then evaporated, the residue heated at 100° for $\frac{1}{2}$ hour, at 180° for 1 minute, cooled, and rubbed with water, and the remaining solid crystallised from toluene and from alcohol. The compound formed pale yellow leaflets, m. p. 141—142° [Found: C, 51.45; H, 4.0; N, 18.2; *M* (in camphor), 240. $C_{10}H_9O_4N_3$ requires C, 51.05; H, 3.85; N, 17.85%; *M*, 235]. Mineral acid readily hydrolysed it to 3-nitrophthalic acid; it was not very soluble in boiling water but after some time went into solution as dimethylhydrazine 3-nitrophthalate, which was isolated in colourless needles.

5-Amino-2 : 3-dimethylphthalaz-1 : 4-dione.—This, prepared from the corresponding nitro-compound by reduction with stannous chloride and concentrated hydrochloric acid at about 50°, separated as the stannichloride, which was decomposed with chalk and water, as described above. The amine (yield, 80%) crystallised from water in anhydrous, very pale yellow, hexagonal prisms, or rhombic needles, m. p. 192° (Found: C, 58.9; H, 5.6. $C_{10}H_{11}O_2N_3$ requires C, 58.5; H, 5.4%), soluble in hot water (1 in 10) or alcohol and very soluble in hot acetic acid; there was some evidence that it formed an unstable hydrate. Its acetyl derivative formed white needles from water or alcohol, m. p. 221—222° (Found: C, 58.2; H, 5.4. $C_{12}H_{13}O_3N_3$ requires C, 58.3; H, 5.3%), and was hydrolysed to the amine by dilute hydrochloric acid. The amine hydrochloride, diazotised and coupled with β -naphthol, gave orange-red needles (from much acetic acid) of the *azo*-compound, m. p. 312—316° (decomp.) (Found: C, 66.5; H, 4.7. $C_{20}H_{16}O_3N_4$ requires C, 66.65; H, 4.45%).

α - and β -6-Nitro-N-methylphthalaz-1 : 4-diones.—4-Nitrophthalic anhydride (4.4 g., freshly crystallised from acetic anhydride) was suspended in glacial acetic acid (20 c.c.) and mixed slowly with methylhydrazine (2.2 g.); the yellow solution was gently boiled under reflux ($\frac{1}{2}$ hour), and the precipitate (3.3 g.) removed while hot; the filtrate, on standing, gave a second crop (1.7 g.). Both crops were mixtures, but the first crop gave the almost pure α -compound after only one crystallisation from acetic acid, and the second crop gave the pure acetyl derivative of the β -isomeride when acetylated and crystallised from acetic acid; from this acetyl derivative the pure β -isomeride was easily obtained by hydrolysis with warm dilute sodium hydroxide solution. The α -nitro-compound formed small, pale greenish-yellow, flat, rhomboidal needles or hexagonal plates (from acetic acid), m. p. 307° (decomp.; sintering from 295°) (Found: C, 48.85; H, 3.3; N, 19.4. $C_9H_7O_4N_3$ requires C, 48.85; H, 3.15; N, 19.0%), and was strongly triboelectric. It formed an orange-red sodium salt, and its acetyl derivative crystallised in small, very pale yellow, square prisms or hexagonal needles, m. p. 210° (previous sintering) (Found: C, 50.5; H, 3.75. $C_{11}H_9O_5N_3$ requires C, 50.2; H, 3.4%), and was easily hydrolysed by dilute sodium hydroxide solution. The β -nitro-compound formed bushes of saffron-yellow pointed prisms (from acetic acid), m. p. 293° (decomp.; sintering from 285°) (Found: C, 48.7; H, 3.55; N, 19.2%), and was only feebly triboelectric; it depressed the m. p. of the α -isomeride to about 255°. The sodium salt formed red needles. The acetyl derivative crystallised in very pale yellow, chisel-ended needles (from acetic acid), m. p. 195° (decomp.; sintering from 185°) (Found: C, 50.15; H, 3.6%), and depressed the m. p. of the α -isomeride to about 170°.

α - and β -6-Amino-N-methylphthalaz-1 : 4-dione.—These amines were prepared by reduction of the corresponding nitro-compounds by means of tin and hydrochloric acid, as described in the preparation of the 5-amino-isomerides; the reduction of the β -nitro-compound was the more rapid, but the stannichloride showed less tendency to separate; the stannichloride of the α -amino-compound formed long, thin, colourless needles. The α -amino-compound formed nearly colourless, rectangular needles (from acetic acid), m. p. 320° (decomp.) (Found: C, 56.3; H, 4.75. $C_9H_9O_2N_3$ requires C, 56.55; H, 4.7%), when crystallised from water, it separated in rectangular needles of a hydrate which retained $1H_2O$ when dried over phosphoric oxide but lost it at 100°; it was soluble in aqueous alkalis, but sparingly soluble in alcohol. The β -amino-isomeride crystallised from much water in short, rectangular, nearly colourless needles, which became anhydrous when dried over phosphoric oxide; m. p. above 360° (decomp.) (Found: C, 56.55; H, 4.75%). It was soluble in aqueous alkali, and its solution in dilute hydrochloric acid had a feeble blue fluorescence. The mixed m. p. of these two isomerides is 305—310° (decomp.).

6-Nitro-2 : 3-dimethylphthalaz-1 : 4-dione.—Prepared by the method described for its 5-nitro-isomeride, this compound formed saffron-yellow dendritic needles (from alcohol), m. p. 198—199° [Found: C, 50.9; H, 4.1; N, 18.0; *M* (in camphor), 241. $C_{10}H_9O_4N_3$ requires C, 51.05; H, 3.85; N, 17.85%; *M*, 235], readily soluble in acetic acid but only sparingly in water or alcohol. It was slowly hydrolysed by hot hydrochloric acid to 4-nitrophthalic acid and *s*-dimethylhydrazine.

6-Amino-2 : 3-dimethylphthalaz-1 : 4-dione.—This was prepared (yield, 80%) in the same way as its 5-amino-isomeride; it crystallised from water in colourless needles of the *dihydrate*, which lost its water at 100° (Found : H₂O, 14.95. C₁₀H₁₁O₂N₃·2H₂O requires H₂O, 14.95%). The anhydrous *amine* formed white rhombs from alcohol, m. p. 262—263° (Found : C, 58.5; H, 6.0. C₁₀H₁₁O₂N₃ requires C, 58.5; H, 5.4%). Its *acetyl* derivative crystallised from water in colourless stout prisms of the *monohydrate*, m. p. 269—270° (Found : C, 54.75; H, 5.75. C₁₂H₁₃O₃N₃·H₂O requires C, 54.35; H, 5.65%). The amine hydrochloride on diazotisation and coupling with β-naphthol gave the *azo*-compound in light red needles (precipitated from acetic acid by addition of hot alcohol), m. p. 270—272° (Found : C, 66.25; H, 4.6. C₂₀H₁₆O₃N₄ requires C, 66.65; H, 4.45%).

4-Nitro-N-dimethylaminophthalimide.—4-Nitrophthalic anhydride (3.5 g.) and *as*-dimethylhydrazine (1.15 g.) were mixed and heated with stirring for 1 hour at 100° and for a minute at 180°; the product was boiled with water and the insoluble crystals (2.3 g.) were recrystallised from alcohol. The *compound* formed saffron-yellow, chisel-ended needles, m. p. 152—153° [Found : C, 50.85; H, 3.8; N, 17.9; *M* (in camphor) 238. C₁₀H₉O₄N₃ requires C, 51.05; H, 3.85; N, 17.85%; *M*, 235], only slightly soluble in water but readily in acetic acid. It was stable to boiling water, but was readily hydrolysed by hot 2*N*-hydrochloric acid.

We thank H.M. Department of Scientific and Industrial Research and the Chemical Society for grants.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON), E. I.
THE TECHNICAL COLLEGE, BIRMINGHAM.

[Received, October 14th, 1936.]
