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1. *New Syntheses of Heterocyclic Compounds. Part XIII.* Some 10-Amino-1 : 3-dimethyl-2 : 9-diazaphenanthrenes.†*

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Methods for the preparation of 2 : 9-diazaphenanthrenes, developed in Part VII of this series, have been extended to include the corresponding 10-amino-4-cyano- and 4-acetyl-10-methyl derivatives.

BIOLOGICAL study of the diazaphenanthrenes described in Parts V and VII of this series (Petrow, *J.*, 1946, 200, 884) has revealed that certain of these compounds show marked analeptic properties (Thorp, Thesis, London, 1947). It was, therefore, of interest to extend the chemistry of this group of compounds in order to throw further light on the structural features associated with this type of biological action. With this object in view, we have applied the synthetic methods developed in Part VII to the preparation of some new 10-amino-4-cyano-2 : 9-diazaphenanthrenes † (IV; R′ = CN, R = NH_2). In addition, we have elaborated a route whereby derivatives of the hitherto unknown 10-methyl-2 : 9-diazaphenanthrene may be obtained.

The preparation of 4-aryl-3 : 5-dicyano-2 : 6-dimethyldihydropyridines (cf. II) had been described by Meyer (*J. pr. Chem.*, 1895, **52**, 101; 1908, **78**, 507) and Mohr (*ibid.*, 1897, **56**, 124), who obtained such compounds by condensing β-aminocrotonitrile with an aryl aldehyde in acidified ethanolic solution (cf. I). When *o*-nitrobenzaldehyde was employed for this purpose only moderate yields (*ca.* 20%) of the resulting 3 : 5-dicyano-1 : 4-dihydro-2 : 6-dimethyl-4-*o*-nitrophenylpyridine (II) were obtained. Systematic study of the reaction conditions, however, revealed that the yield of required material could be raised to 88% by carrying out the condensation in glacial acetic acid solution, and this improved procedure was employed throughout the investigation. In this way, the corresponding 4-*o*-nitrophenyl-2 : 6-diphenyl, 4-(2 : 4-dinitrophenyl)-2 : 6-dimethyl, 4-(2 : 4-dinitrophenyl)-2 : 6-diphenyl, 4-(4-hydroxy-3-methoxy-2-nitrophenyl)-2 : 6-dimethyl, and 4-(4-hydroxy-3-methoxy-2-nitrophenyl)-2 : 6-diphenyl analogues of (II) were readily obtained.

Oxidation of the foregoing 1 : 4-dihydropyridines to the corresponding pyridines (cf. III) was effected by means of dilute nitric acid, or, better, by chromic acid in hot acetic acid solution or suspension (Meyer, *J. pr. Chem.*, 1915, **92**, 175). Phenolic groups were protected by acetylation before oxidation. Yields were uniformly good.

Reductive cyclisation of (III) with reduced iron in acidulated aqueous-ethanolic solution surprisingly failed to give 10-amino-4-cyano-1 : 3-dimethyl-2 : 9-diazaphenanthrene (cf. IV; R = NH_2, R′ = CN), a result in marked contrast to observations recorded in Part VII. The latter compound was ultimately obtained by performing the reduction with hot sodium dithionite (hydrosulphite) solution. Reductive cyclisation of the remaining *o*-nitrophenylpyridines likewise required individual study of each compound, the 10-amino-4-cyano-2 : 9-diazaphenanthrenes being obtained by use of the reducing agents indicated : 1 : 3-diphenyl- (stannous chloride), 7-amino-1 : 3-dimethyl- (reduced iron), 7-acetoxy-8-methoxy-1 : 3-dimethyl- (reduced iron), 7-acetoxy-8-methoxy-1 : 3-diphenyl- (reduced

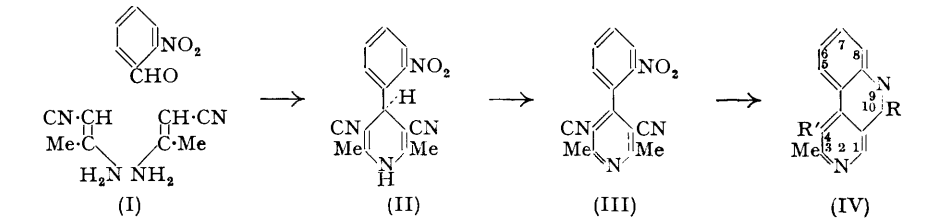
* Part XII, *J.*, 1951, 551.

† Referred to as 7 : 10-diazaphenanthrenes in Part VII for reasons outlined in Part V.

iron). Experiments on the reductive cyclisation of 3 : 5-dicyano-4-(2 : 4-dinitrophenyl)-2 : 6-diphenylpyridine proved inconclusive.

The preparation of a 9-methyl-2 : 10-diazaphenanthrene has been described in Part V (*loc. cit.*). Some isomeric 10-methyl-2 : 9-diazaphenanthrenes (IV; R = Me) have now been prepared by reductive cyclisation of suitably constituted 3 : 5-diacetyl-4-*o*-nitrophenylpyridines (VIII), which were obtained by means of a Knoevenagel extension of the Hantzsch synthesis.

Ruhemann (*J.*, 1903, **83**, 1373) has shown that *m*-nitrobenzaldehyde reacts with acetylacetone, in the presence of piperidine as catalyst, to give *m*-nitrobenzylideneacetylacetone. By use of *o*-nitrobenzaldehyde, *o*-nitrobenzylideneacetylacetone (VI) has been obtained in nearly quantitative yield. The latter compound (VI) has now been found to undergo facile condensation with 4-aminopent-3-en-2-one (the " ammonia derivative " of acetylacetone) at 100° to give 3 : 5-diacetyl-1 : 4-dihydro-2 : 6-dimethyl-4-*o*-nitrophenylpyridine (VII). Oxidation of the dihydropyridine with chromium trioxide furnished the corresponding pyridine derivative (VIII), which passed smoothly into 4-acetyl-1 : 3 : 10-trimethyl-2 : 9-diazaphenanthrene on reduction with reduced iron.



Attempts to prepare (VII) by direct condensation of *o*-nitrobenzaldehyde with acetylacetone and its " ammonia " derivative proved unsuccessful, preliminary formation of (VI) being required. With 2-nitrovanillin as the carbonyl component, however, a different situation obtained. In this instance attempts to prepare the initial condensation product corresponding to (VI) were not successful. 3 : 5-Diacetyl-1 : 4-dihydro-4-(4-hydroxy-3-methoxy-2-nitrophenyl)-2 : 6-dimethylpyridine was ultimately prepared in low yield by simply heating the three components in ethanolic solution on the water-bath. Oxidation of its acetyl derivative, followed by reduction, furnished 7-acetoxy-4-acetyl-8-methoxy-1 : 3 : 10-trimethyl-2 : 9-diazaphenanthrene, hydrolysis of which gave the 7-hydroxy-derivative which could be methylated in the usual way.

In addition to studying the reductive ring closure of compounds of types (III) and (VIII), an attempt has been made to extend the work to include some 4-*o*-nitrophenylpyridines possessing two different groups at 3 and 5. Some preliminary experiments in this direction have already been reported in Part VII, in which the conversion of 5-carbethoxy-3-cyano-2 : 6-dimethyl-4-*o*-nitrophenylpyridine into 10-amino-4-carbethoxy-1 : 3-dimethyl-2 : 9-diazaphenanthrene has been described.

Condensation of *o*-nitrobenzylideneacetylacetone with ethyl β-aminocrotonate furnished 5-acetyl-3-carbethoxy-1 : 4-dihydro-2 : 6-dimethyl-4-*o*-nitrophenylpyridine in 42% yield. Oxidation of this compound gave a gummy product which could not be crystallised. It was, therefore, reduced directly with reduced iron to give 5-acetyl-4-*o*-aminophenyl-3-carbethoxy-2 : 6-dimethylpyridine, a relatively stable compound which did not appear to undergo spontaneous ring closure. Treatment with acetic anhydride effected lactam

formation with concomitant acetylation, to give 10-acetoxy-4-acetyl-1 : 3-dimethyl-2 : 9-diazaphenanthrene, which was isolated as the hemihydrate.

Condensation of *o*-nitrobenzylideneacetylacetone with β-aminocrotononitrile gave 5-acetyl 3-cyano-1 : 4-dihydro-2 : 6-dimethyl-4-*o*-nitrophenylpyridine, which could not be obtained analytically pure. Oxidation furnished the pyridine derivative, reduction of which gave an inseparable mixture of products in which the corresponding diazaphenanthrenes appeared to be present.

Experimental

(M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss.)

3 : 5-*Dicyano*-1 : 4-*dihydro*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine* (II).—A solution of *o*-nitrobenzaldehyde (4·5 g.) and β-aminocrotononitrile (4·9 g.) (Holtzwart, *J. pr. Chem.*, 1889, **39**, 230) in glacial acetic acid (25 ml.) was heated under reflux for 15 minutes. Separation of solid began almost immediately. After cooling, the solids were collected and crystallised from absolute ethanol, to give the *dicyano*-compound (II), canary-yellow needles, m. p. 216—217° (Found : C, 63·5; H, 4·8; N, 19·9. $C_{15}H_{12}O_2N_4$ requires C, 64·3; H, 4·3; N, 20·0%).

3 : 5-*Dicyano*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine* (III).—The foregoing compound (4 g.) in hot acetic acid (20 ml.) was oxidised with chromic acid (1 g.) dissolved in a little water and added dropwise with stirring. 3 : 5-*Dicyano*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine* separated on cooling in nearly quantitative yield and, after crystallisation from aqueous ethanol, formed faintly yellow needles, m. p. 146·5—147·5° (Found : C, 64·8; H, 3·4; N, 19·7. $C_{15}H_{10}O_2N_4$ requires C, 64·8; H, 3·6; N, 20·1%).

10-*Amino*-4-*cyano*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene*.—The foregoing compound (2 g.) was finely powdered and added in one portion to a hot concentrated solution (25 ml.) of sodium dithionite (hydrosulphite). After 2 hours on the water-bath the cooled mixture was extracted with chloroform, and the extract evaporated to dryness. Crystallisation from absolute ethanol gave 10-*amino*-4-*cyano*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* (47%), light yellow needles, m. p. 273° (Found : C, 72·5; H, 5·1; N, 22·4. $C_{15}H_{12}N_4$ requires C, 72·6; H, 4·8; N, 22·6%). The compound failed to give the primary amine test on diazotisation and coupling with alkaline β-naphthol, a behaviour characteristic of this type of compound (cf. Parts V and VII, *locc. cit.*).

3 : 5-*Dicyano*-1 : 4-*dihydro*-4-o-*nitrophenyl*-2 : 6-*diphenylpyridine*.—This was prepared by condensing *o*-nitrobenzaldehyde (3 g.) and β-aminocinnamonitrile (6 g.) (Holtzwart, *loc. cit.*) in glacial acetic acid (25 ml.) under reflux, in nearly quantitative yield and had m. p. 258° (cf. Meyer, *J. pr. Chem.*, 1908, **78**, 512).

3 : 5-*Dicyano*-4-o-*nitrophenyl*-2 : 6-*diphenylpyridine*.—The foregoing dihydro-compound (5·9 g.) was finely powdered and suspended in hot acetic acid (100 ml.). To it, chromium trioxide (1·2 g.) dissolved in water (*ca.* 5 ml.) was rapidly added in one portion. The dihydro-base went rapidly into solution, and 3 : 5-*dicyano*-4-o-*nitrophenyl*-2 : 6-*diphenylpyridine* immediately separated in nearly quantitative yield, as felted white needles (from glacial acetic acid), m. p. 232—233° (Found : C, 74·7; H, 3·6; N, 13·8. $C_{25}H_{14}O_2N_4$ requires C, 74·6; H, 3·5; N, 13·9%).

10-*Amino*-4-*cyano*-1 : 3-*diphenyl*-2 : 9-*diazaphenanthrene*.—The foregoing compound (2 g.) was suspended in a mixture of concentrated hydrochloric acid (80 ml.) and glacial acetic acid (40 ml.) and treated with stannous chloride dihydrate (16 g.). The mixture was then heated on the water-bath until all the original base had disappeared and had been replaced by a yellow crystalline deposit. After being kept overnight, the product was collected, digested with excess of concentrated sodium hydroxide solution, and allowed to cool. The precipitated solids, on crystallisation from pyridine, yielded 10-*amino*-4-*cyano*-1 : 3-*diphenyl*-2 : 9-*diazaphenanthrene*, felted, golden-yellow needles, m. p. 276—277° (Found : C, 80·2; H, 4·4; N, 15·3. $C_{25}H_{16}N_4$ requires C, 80·6; H, 4·3; N, 15·1%). The compound formed a sparingly soluble hydrochloride which failed to give a primary amine test on diazotisation.

3 : 5-*Dicyano*-1 : 4-*dihydro*-4-(2 : 4-*dinitrophenyl*)-2 : 6-*dimethylpyridine*, obtained in nearly quantitative yield, formed lemon-yellow needles, m. p. 268—270° (decomp.), on crystallisation from a very large volume (300 pts.) of glacial acetic acid (Found : C, 55·6; H, 3·5; N, 21·2. $C_{15}H_{11}O_4N_5$ requires C, 55·4; H, 3·4; N, 21·5%).

3 : 5-*Dicyano*-4-(2 : 4-*dinitrophenyl*)-2 : 6-*dimethylpyridine* (78%) separated from absolute ethanol in faintly yellow pyramids, m. p. 159·5° (Found : C, 55·3; H, 2·9; N, 21·4. $C_{15}H_9O_4N_5$ requires C, 55·5; H, 2·8; N, 21·7%).

7 : 10-*Diamino*-4-*cyano*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene*.—The foregoing compound

(1 g.) was heated under reflux for 1 hour with ethanol (30 ml.) containing 3 drops of concentrated hydrochloric acid and reduced iron (3 g.). After removal of solids a few drops of ammonia solution (*d* 0·88) were added, and the mixture was boiled and filtered. Concentration to small bulk gave 7 : 10-*diamino*-4-*cyano*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene hemihydrate*, deep yellow crystals, m. p. 288—289° (decomp.) (Found : C, 66·1; H, 5·1; N, 25·0. $C_{15}H_{13}N_5,\frac{1}{2}H_2O$ requires C, 66·2; H, 5·1; N, 25·1%).

3 : 5-*Dicyano*-4-(2 : 4-*dinitrophenyl*)-1 : 4-*dihydro*-2 : 6-*diphenylpyridine*.—2 : 4-Dinitrobenzaldehyde (4 g.), β-aminocinnamonitrile (6 g.), and glacial acetic acid (25 ml.) were heated under reflux for 1 hour. Addition of water precipitated an orange gum which solidified in contact with absolute ethanol (10 ml.). Crystallisation from absolute ethanol or glacial acetic acid gave 3 : 5-*dicyano*-4-(2 : 4-*dinitrophenyl*)-1 : 4-*dihydro*-2 : 6-*diphenylpyridine* (45%), small yellow plates, m. p. 218° (Found : C, 66·8; H, 3·2; N, 15·7. $C_{25}H_{15}O_4N_5$ requires C, 66·8; H, 3·3; N, 15·6%). 3 : 5-*Dicyano*-4-(2 : 4-*dinitrophenyl*)-2 : 6-*diphenylpyridine*, obtained in nearly quantitative yield, formed colourless needles (from absolute ethanol), m. p. 211° (Found : C, 66·7; H, 2·8; N, 15·6. $C_{25}H_{13}O_4N_5$ requires C, 67·1; H, 2·9; N, 15·6%). Catalytic reduction of this compound (1 g.) in absolute ethanol (300 ml.) in the presence of palladised charcoal (0·75 g.) gave small orange needles, m. p. >300° (Found, in 4 samples : C, 68·0—70·4; H, 4·1—4·4; N, 14·1—15·2%).

3 : 5-*Dicyano*-1 : 4-*dihydro*-4-(4-*hydroxy*-3-*methoxy*-2-*nitrophenyl*)-2 : 6-*dimethylpyridine*, obtained (70%) from 2-nitrovanillin (Stoessen, *J. Amer. Chem. Soc.*, 1928, **50**, 2559), separated from glacial acetic acid in faintly yellow needles, m. p. 266° (decomp.) (Found : C, 58·9; H, 4·3; N, 17·2. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·3; N, 17·2%). 4-(4-*Acetoxy*-3-*methoxy*-2-*nitrophenyl*)-3 : 5-*dicyano*-1 : 4-*dihydro*-2 : 6-*dimethylpyridine*, obtained (80%) by acetylation of the foregoing compound (2 g.) with acetic anhydride (15 ml.) for 30 minutes under reflux, formed pale yellow needles, m. p. 214°, from glacial acetic acid (Found : C, 58·8; H, 4·5. $C_{18}H_{16}O_5N_4$ requires C, 58·7; H, 4·3%). 4-(4-*Acetoxy*-3-*methoxy*-4-*nitrophenyl*)-3 : 5-*dicyano*-2 : 6-*dimethylpyridine*, obtained (80%) by oxidation of the foregoing compound, formed large glistening plates (from absolute ethanol), m. p. 190·5° (Found : C, 59·0; H, 4·2; N, 15·3. $C_{18}H_{14}O_5N_4$ requires C, 59·0; H, 3·8; N, 15·3%). 7-*Acetoxy*-10-*amino*-4-*cyano*-8-*methoxy*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene*, obtained (80%) by reducing the foregoing compound with reduced iron, formed lemon-yellow needles (from ethanol), m. p. 239° (Found : C, 64·7; H, 4·7; N, 16·4. $C_{18}H_{16}O_3N_4$ requires C, 64·3; H, 4·8; N, 16·7%).

3 : 5-*Dicyano*-1 : 4-*dihydro*-4-(4-*hydroxy*-3-*methoxy*-2-*nitrophenyl*)-2 : 6-*diphenylpyridine* separated (70%) from glacial acetic acid in very small phototropic crystals, m. p. 279° (Found : C, 67·9; H, 4·1; N, 12·2. $C_{26}H_{18}O_4N_4,\frac{1}{2}H_2O$ requires C, 68·0; H, 4·1; N, 12·2%). Its *acetyl* derivative (82%) formed long, pale-yellow needles (from absolute ethanol), m. p. 242° (Found : C, 67·9; H, 4·4. $C_{28}H_{20}O_5N_4$ requires C, 68·3; H, 4·1%).

4-(4-*Acetoxy*-3-*methoxy*-2-*nitrophenyl*)-3 : 5-*dicyanopyridine* (70%) separated from alcohol in small needles, m. p. 184—185° (Found : C, 69·0; H, 3·6; N, 11·4. $C_{28}H_{18}O_5N_4$ requires C, 68·6; H, 3·7; N, 11·4%).

7-*Acetoxy*-10-*amino*-4-*cyano*-1-*methoxy*-1 : 3-*diphenyl*-2 : 9-*diazaphenanthrene* (>90%) crystallised from ethanol in pale-yellow needles, m. p. 253° (Found : C, 73·0; H, 4·4; N, 12·3. $C_{28}H_{20}O_3N_4$ requires C, 73·0; H, 4·3; N, 12·1%).

o-*Nitrobenzylideneacetylacetone* (VI), obtained by leaving a solution of powdered *o*-nitrobenzaldehyde (7·5 g.) in acetylacetone (5 g.) containing a little piperidine for 2 days in a desiccator, formed pale yellow plates, m. p. 75·5—76·5°, from ethanol (Found : C, 61·8; H, 4·9; N, 5·7. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7; N, 6·0%).

3 : 5-*Diacetyl*-1 : 4-*dihydro*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine* (VII).—The foregoing compound (7·5 g.) and 4-aminopent-3-en-2-one (6·5 g.) (Combes and Combes, *Bull. Soc. chim.*, 1892, **7**, 779) were heated together on the water-bath for 12 hours. The partly crystalline product obtained was freed from oily material by addition of methanol (10 ml.), the solids being collected after 12 hours and crystallised from a little ethanol. The *diacetyl* compound (VII) (32%) formed phototropic yellow needles, m. p. 226·5—227·5° (Found : C, 64·6; H, 5·6; N, 8·8. $C_{17}H_{18}O_4N_2$ requires C, 65·0; H, 5·1; N, 8·9%). Addition of a few drops of piperidine to the reaction mixture lowered the yield to 27%. The corresponding *pyridine* (VIII) (>95%) formed nearly colourless needles (from aqueous alcohol), m. p. 142·5—143·5° (Found : N, 9·3. $C_{17}H_{16}O_4N_2$ requires N, 9·0%).

4-*Acetyl*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene* (IV; R = Me, R′ = Ac) (45—50%), spear-head-shaped crystals from ligroin, had m. p. 166—167° (Found : C, 77·5; H, 5·7; N, 10·4. $C_{17}H_{16}ON_2$ requires C, 77·3; H, 6·0; N, 10·6%).

3 : 5-*Diacetyl*-1 : 4-*dihydro*-4-(4-*hydroxy*-3-*methoxy*-2-*nitrophenyl*)-2 : 6-*dimethylpyridine*, prepared (21%) by heating 2-nitrovanillin (19 g.), acetylacetone (12·5 ml.), and 4-aminopent-3-en-2-one (12·5 ml. in (ethanol (60 ml.) in an open flask on the water-bath for 2 days, followed by stirring with cold methanol (60 ml.), formed ivory needles from ethanol; it had m. p. 246—247° (decomp.) (Found : C, 59·8; H, 5·5; N, 7·5. $C_{18}H_{20}O_6N_2$ requires C, 60·0; H, 5·6; N, 7·8%). It failed to give a colour with ferric chloride. Its *acetyl* derivative formed very small needles (from acetic acid), m. p. 254·5—255·5° (decomp.) (Found : C, 59·3; H, 5·3; N, 6·3. $C_{20}H_{22}O_7N_2$ requires C, 59·7; H, 5·5; N, 7·0%).

4-(4-*Acetoxy*-3-*methoxy*-2-*nitrophenyl*)-3 : 5-*diacetyl*-2 6-*dimethylpyridine* (69%), plates from aqueous acetone, had m. p. 152·5—153·5° (Found : C, 60·0; H, 4·7; N, 7·3. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0; N, 7·0%).

7-*Acetoxy*-4-*acetyl*-8-*methoxy*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene* (82%) was obtained in faintly yellow plates, m. p. 153·5—154·5° (Found : C, 68·4; H, 5·6; N, 7·5. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%). 4-*Acetyl*-7-*hydroxy*-8-*methoxy*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene*, prepared by hydrolysis of the foregoing compound with 10% potassium hydroxide solution (10 vols.) followed by precipitation with carbon dioxide, formed octahedra from ethanol–ligroin and had m. p. 202—203° (Found : C, 70·0; H, 5·5; N, 9·0. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8; N, 9·0%). 4-*Acetyl*-7 : 8-*dimethoxy*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene*, prepared by methylating the foregoing compound (1·5 g.) in water (20 ml.) and potassium hydroxide (280 mg.) with methyl sulphate (630 mg.), formed octahedra (from aqueous methanol), m. p. 136—137° (Found : C, 70·3; H, 6·0; N, 8·8. $C_{19}H_{20}O_3N_2$ requires C, 70·6; H, 6·2; N, 8·7%).

5-*Acetyl*-3-*carbethoxy*-1 : 4-*dihydro*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine*, prepared (42%) by heating ethyl β-aminocrotonate (4·5 g.) with *o*-nitrobenzylideneacetylacetone (6·9 g.) for 2 days on the water-bath, formed yellow phototropic prisms from aqueous ethanol; it had m. p. 175·5—176·5° (Found : C, 62·8; H, 5·8; N, 7·8. $C_{18}H_{20}O_5N_2$ requires C, 62·8; H, 5·8; N, 8·1%). The corresponding *pyridine*, prepared by oxidation of the dihydropyridine with chromium trioxide, followed by reduction of the resulting product with reduced iron, was obtained in faintly green small crystals, m. p. 152—153°, from chloroform–light petroleum (Found : C, 69·4; H, 5·9; N, 9·0. $C_{18}H_{20}O_3N_2$ requires C, 69·5; H, 6·4; N, 9·0%). An acidified solution of this compound, on treatment with nitrous acid at 0°, did not couple immediately with alkaline β-naphthol, but slowly developed a red colour.

10-*Acetoxy*-4-*acetyl*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene*, prepared (81%) by heating the foregoing compound (2 g.) with acetic anhydride (10 ml.) under reflux for 3 minutes and pouring on crushed ice (50 g.), formed plates, m. p. 134°, from ethanol or benzene (Found : C, 68·3; H, 5·8; N, 8·2. $C_{17}H_{16}O_3N_2,\frac{1}{2}H_2O$ requires C, 68·1; H, 5·4; N, 8·8%).

5-*Acetyl*-3-*cyano*-1 : 4-*dihydro*-2 : 6-*dimethyl*-4-o-*nitrophenylpyridine*, prepared from β-aminocrotononitrile (4·1 g.) and *o*-nitrobenzylideneacetylacetone (11·5 g.), separated from aqueous acetic acid in phototropic golden needles, m. p. 213—214° (Found : C, 63·4; H, 5·3; N, 14·7. $C_{16}H_{15}O_3M_3$ requires C, 64·7; H, 5·1; N, 14·1%). The corresponding *pyridine* formed rhombic crystals (from methanol), m. p. 117·5—118·5° (Found : C, 65·3; H, 4·3; N, 14·5. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·4; N, 14·2%).

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