Polyazaheterocyclic Compounds: Condensation Reactions of Pyridazine-4,5-dicarboxylic Acid Derivatives with *o*-Phenylenediamine

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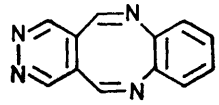
Diethyl pyridazine-4,5-dicarboxylate (II) and its 3,6-dimethyl derivative (XIV) cyclised with *o*-phenylenediamine in the presence of sodium hydride to give 6,11-dihydropyridazino[4,5-*c*][1,6]benzodiazocine-5,12-dione (III) and its 1,4-dimethyl derivative (XV), respectively. By heating under reduced pressure these compounds were dehydrated to the corresponding pyridazino[4',5':3,4]pyrrolo[1,2-*a*]benzimidazol-11-ones (XII) and (XX).

Compound (III) reacted with diazomethane yielding a mixture of di-*N*-methyl (IV), *NO*-dimethyl (V), and di-*O*-methyl (VI) derivatives. Mild alkaline hydrolysis of the dione (III) afforded 5-(*o*-aminophenylcarbamoyl)-pyridazine-4-carboxylic acid (VII), which cyclised to 5-(benzimidazol-2-yl)pyridazine-4-carboxylic acid (VIII). Heating compound (III) with hexamethylphosphoric triamide gave *NN*-dimethyl-5-(benzimidazol-2-yl)pyridazine-4-carboxamide (XI).

3,6-Dimethylpyridazine-4,5-dicarboxylic anhydride (XVI) reacted with *o*-phenylenediamine at room temperature to give 3,6-dimethyl-5-(*o*-aminophenylcarbamoyl)pyridazine-4-carboxylic acid (XVII), whereas when refluxed with the same reagent in acetic acid it afforded 2-(3,6-dimethylpyridazin-4-yl)benzimidazole (XVIII).

REACTIONS of suitably substituted pyridazines with hydrazine have provided good routes to pyridazino-[4,5-*d*]pyridazine and its derivatives.[1a-d] We describe here attempts to extend this approach to similar reactions with *o*-phenylenediamine, as routes to derivatives of pyridazino[4,5-*c*][1,6]benzodiazocine (I), a new heterocyclic system.



(I)

Diethyl pyridazine-4,5-dicarboxylate (II) did not react with *o*-phenylenediamine even on prolonged refluxing in tetrahydrofuran. However, if the reaction was carried out in the presence of sodium hydride [2] 6,11-dihydropyridazino[4,5-*c*][1,6]benzodiazocine-5,12-dione (III) was obtained, identified on the basis of analytical, spectroscopic, and chemical properties. The i.r. spectrum shows two strong bands at 1675 and 1657 cm^{-1} and a broad pattern between 3300 and 2600 cm^{-1} (maxima at 3170 and 3070 cm^{-1}) attributable to –CO–NH– groups. N.m.r. data are given in the Table.

Compound (III) was soluble in alkali and insoluble in acids; it reacted with diazomethane to give a quantitative yield of three dimethyl derivatives, separated by preparative t.l.c. N.m.r. evidence (Table) led us to formulate the two main products of the reaction as the di-*N*-methyl (IV) and the *NO*-dimethyl (V) derivatives; the third isomer was assigned the di-*O*-methyl structure (VI).

The dione (III) gave pyridazine-4,5-dicarboxylic acid and *o*-phenylenediamine on refluxing in alkali, but afforded 5-(*o*-aminophenylcarbamoyl)pyridazine-4-carboxylic acid (VII) when the hydrolysis was carried out at lower temperature. Compound (VII) cyclised on heating in methanol to give the benzimidazolylpyridazinecarboxylic acid (VIII) as main product. The i.r. (see Experimental section) and n.m.r. spectra (Table) were consistent with a zwitterionic structure, probably of the type (VIIIa).

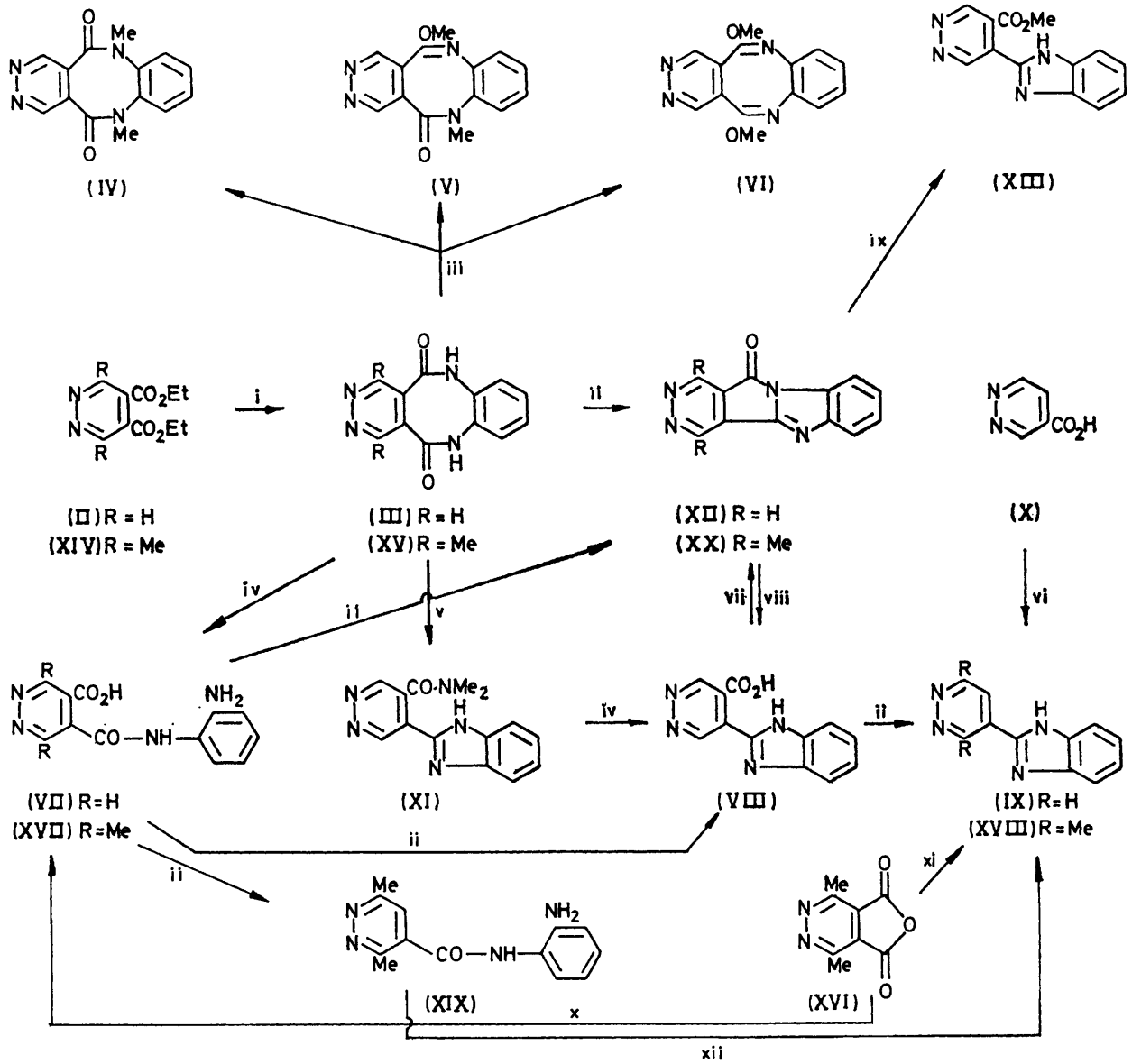
On heating *in vacuo* the acid (VIII) was decarboxylated; the product (IX) was also obtained by condensation of pyridazine-4-carboxylic acid (X) with *o*-phenylenediamine in polyphosphoric acid. In the n.m.r. spectrum of compound (IX) the pyridazine ring protons give rise to an AMX pattern. The signals were assigned by comparison with the corresponding chemical shifts and coupling constants of pyridazine; [3] the considerable paramagnetic effect on the 3- and 5-protons must be ascribed to the benzimidazole ring.

On heating with hexamethylphosphoric triamide, compound (III) predominantly gave the benzimidazolylpyridazine (XI). Its i.r. spectrum shows a broad band between 3400 and 2500 cm^{-1} (NH) and a strong band at 1650 cm^{-1} attributable to the tertiary amidic CO group. The u.v. spectrum (see Experimental section) closely resembles those of compounds (VIII) and (IX); the n.m.r. spectrum (Table) strongly supported the assigned structure.

Scheme 2 shows two possible mechanisms (a and b) for the formation of compound (XI), based on the reported behaviour of hexamethylphosphoric triamide with alcohols and amides.[4,5] Since the reaction temperature is high enough (210—215°), the suggested intermediate (XII) (route b) could also arise directly from compound (III) (see below). On heating with alkali the amide (XI) was hydrolysed to the acid (VIII).

The diazocine derivative (III) largely decomposed when heated above 240° at atmospheric pressure, whereas it sublimed unchanged at 170—180° and 0·05 mmHg. However, if the sublimation was carried out at 200—210° and 15—20 mmHg, it was possible to isolate pyridazino-[4',5':3,4]pyrrolo[1,2-*a*]benzimidazol-11-one (XII), which was also obtained in higher yield by cyclisation of the acid (VIII) with boiling acetic anhydride. The i.r. spectrum, showing a strong double band at 1767 and 1744 cm^{-1} for the CO group (splitting may be due to Fermi

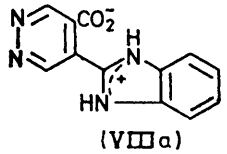
[1] G. Adembri, F. De Sio, R. Nesi, and M. Scotton, (*a*) *Chem. Comm.*, 1967, 1006; (*b*) *J. Chem. Soc.* (*C*), 1968, 2857; (*c*) *ibid.*, 1970, 1536; (*d*) *Chimica e Industria*, 1970, **52**, 507.
[2] W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, 1969, **34**, 2138.
[3] J. A. Elvidge and P. D. Ralph, *J. Chem. Soc.* (*B*), 1966, 249.
[4] R. S. Monson, *Tetrahedron Letters*, 1971, 567.
[5] R. S. Monson and D. N. Priest, *Canad. J. Chem.*, 1971, **49**, 2897.



SCHEME 1 Reagents: i, o-$(NH_2)_2C_6H_4$–NaH; ii, heat; iii, CH_2N_2; iv, NaOH; v, $OP(NMe_2)_3$; vi, o-$(NH_2)_2C_6H_4$–polyphosphoric acid; vii, $(Ac)_2O$; viii, H_2O; ix, MeOH; x, o-$(NH_2)_2C_6H_4$ in tetrahydrofuran at room temperature; xi, o-$(NH_2)_2C_6H_4$ in boiling AcOH; xii, polyphosphoric acid

resonance), and the n.m.r. spectrum (Table) are in agreement with the assigned structure.

The tetracyclic derivative (XII) reacted with water and methanol to give the acid (VIII) and the ester (XIII), respectively.



(VIIIa)

Diethyl 3,6-dimethylpyridazine-4,5-dicarboxylate (XIV) cyclised with o-phenylenediamine in the presence of sodium hydride to the 1,4-dimethylpyridazinobenzodiazocinedione (XV). In contrast, from the anhydride (XVI) with o-phenylenediamine we never obtained the dione (XV); if the reaction was carried out at room temperature, compound (XVI) gave the acid (XVII) in quantitative yield, whereas in boiling acetic acid it afforded the benzimidazole (XVIII) as main product. The structure of the latter compound followed from n.m.r. evidence.

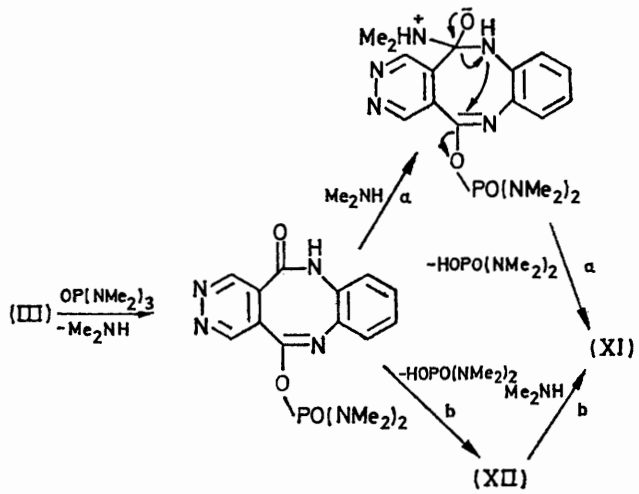
Compound (XVII) behaved differently from the corresponding acid (VII); when refluxed in methanol it mainly decarboxylated to the amide (XIX), identified on the basis of the i.r. (see Experimental section) and n.m.r. spectra (Table), and its cyclisation to the derivative (XVIII).

Sublimation of the acid (XVII) at 175° and 0·03 mmHg gave a crude product from which we isolated 1,4-dimethylpyridazino[4′,5′:3,4]pyrrolo[1,2-a]benzimidazol-11-one (XX), also prepared by heating the diazocine (XV) under reduced pressure.

N.m.r. spectra (60 MHz; δ values, J in Hz; internal tetramethylsilane as reference)

Compd.	Solvent	Proton resonance	Assignment
(III)	$(CD_3)_2SO$	7·25s	ArH_4
		9·30s	1-, 4-H
		10·73br, s	2 × NH
(IV)	$CDCl_3$	3·48s	2 × NMe
		7·28s	ArH_4
		9·12s	1-, 4-H
(V)	$CDCl_3$	3·38s	NMe
		4·06s	OMe
		6·75—7·30m	ArH_4
		9·03d, 9·24d } $J_{1,4}$ 1	1-, 4-H
(VI)	$CDCl_3$	4·05s	2 × OMe
		6·96s	ArH_4
		9·16s	1-, 4-H
(VIII)	$(CD_3)_2SO$	7·55m [b]	ArH_4
		8·30br, s [a]	2 × NH+
		9·60d, 9·88d } $J_{3,6}$ 1	3-, 6-H
(IX)	$(CD_3)_2SO$	7·53m [b]	ArH_4
		8·30dd $J_{3,5}$ 2·3	5-H
		9·46dd $J_{3,6}$ 1·1	6-H
		9·97dd $J_{5,6}$ 5·4	3-H
(XI)	$(CD_3)_2SO$	2·74s, 3·09s [c]	NMe_2
		7·49m [b]	ArH_4
		9·31d, 9·88d } $J_{3,6}$ 1	3-H, 6-H
(XII)	$CDCl_3$	7·30—8·20m	ArH_4
		9·58d, 9·80d } $J_{1,4}$ 1·8	1-, 4-H
(XIII)	$(CD_3)_2SO$	3·91s	Me
		7·55m [b]	ArH_4
		9·57d, 9·94d } $J_{3,6}$ 1	3-H, 6-H
(XV)	$(CD_3)_2SO$	2·61s	1-, 4-Me
		7·32s	ArH_4
		10·8br, s [a]	2 × NH
(XVIII)	$(CD_3)_2SO$	2·7s	6-Me
		3·0s	3-Me
		7·55m [b]	ArH_4
		7·97s	5-H
(XIX)	$(CD_3)_2SO$	2·65s, 2·68s	3-, 6-Me
		5·0br, s [a]	NH_2
		6·5—7·4m	ArH_4
		7·75s	5-H
		9·81br, s [a]	NH
(XX)	$CDCl_3$	3·08s, 3·17s	1-, 4-Me
		7·2—8·1m	ArH_4

Signal disappears on deuteriation. [b] Middle value of a symmetrical AA'BB' pattern. [c] The two signals coalesce near 126° and give a sharp singlet at about 160°.



SCHEME 2

EXPERIMENTAL

I.r. spectra were measured for dispersions in potassium bromide with a Perkin-Elmer 457 spectrometer. ^1H N.m.r. spectra were recorded with a Varian A-56/60 instrument; chemical shifts are reported in p.p.m. downfield from internal tetramethylsilane. Unless otherwise stated, u.v. spectra were measured for solutions in methanol with a Cary 14 spectrophotometer. The molecular weight of compound (III) was determined mass spectroscopically with a Perkin-Elmer 270 machine. Silica gel plates (Merck F_{254}) were used for analytical and preparative t.l.c.

6,11-Dihydropyridazino[4,5-c][1,6]*benzodiazocine-5,12-dione* (III).—A mixture of diethyl pyridazine-4,5-dicarboxylate (II) [1b] (2 g), *o*-phenylenediamine (0·965 g), and sodium hydride (80% oil dispersion; 0·54 g) in anhydrous tetrahydrofuran (20 ml) was stirred at room temperature for 24 h. Water (100 ml) was added to the mixture and the resulting cooled solution was neutralised with concentrated hydrochloric acid; the mixture was then warmed and acidified (pH 1) to give a solid which was filtered off, dried, and washed with ether (yield 1·45 g, 67·5%). *Compound* (III) crystallised from water as needles, m.p. 250—251° (decomp.) (Found: C, 60·0; H, 3·4; N, 23·2%; M^+, 240. $C_{12}H_8N_4O_2$ requires C, 60·0; H, 3·4; N, 23·3%; M, 240); $\lambda_{max.}$ 206, 262, and 315sh nm (log ε 4·56, 3·69, and 2·73).

Methylation of Compound (III) *with Diazomethane*.—A suspension of compound (HI) (0·2 g) in ether (10 ml) and methanol (10 ml) was treated with an excess of ethereal diazomethane and set aside overnight. Removal of the solvent under reduced pressure left a solid residue (0·21 g) which was sublimed at 110—140° and 0·02 mmHg and resolved into three components by preparative layer chromatography with chloroform–methanol (100 : 1 v/v) as developer.

The fastest running band gave a small amount (0·015 g) of *5,12-dimethoxypyridazino*[4,5-c][1,6]*benzodiazocine* (VI), m.p. 202—204° (from cyclohexane) (Found: C, 62·5; H, 4·5; N, 21·0. $C_{14}H_{12}N_4O_2$ requires C, 62·7; H, 4·5; N, 20·9%); $\lambda_{max.}$ 250sh, 275, and 325sh nm (log ε 3·76, 3·61, and 2·87). The second band yielded *12-methoxy-6-methylpyridazino*[4,5-c][1,6]*benzodiazocin-5*(6H)*-one* (V) (0·06 g), m.p. 148—150° (from cyclohexane) (Found: C, 62·8; H, 4·6; N, 20·7%); $\nu_{max.}$ 1668 cm^{-1} (CO); $\lambda_{max.}$ 208, 260, and 305sh nm (log ε 4·47, 3·68, and 3·01). The slowest-running band afforded *6,11-dihydro-6,11-dimethylpyridazino*[4,5-c]-[1,6]*benzodiazocine-5,12-dione* (IV) (0·075 g), m.p. 223—225° (from benzene) (Found: C, 62·6; H, 4·5; N, 20·7%); $\nu_{max.}$ 1660 cm^{-1} (CO); $\lambda_{max.}$ 210, 263, and 320sh nm (log ε 4·42, 3·64, and 2·32).

Alkaline Hydrolysis of Compound (III).—(*a*) A solution of compound (III) (0·2 g) in aqueous sodium hydroxide (10%; 2 ml) was refluxed for 8 h. The mixture was cooled and extracted with chloroform (2 × 5 ml); evaporation of the dried extracts gave *o*-phenylenediamine (0·08 g). Strong acidification of the alkaline solution with concentrated hydrochloric acid precipitated pyridazine-4,5-dicarboxylic acid (0·07 g), identical (m.p. and i.r. spectrum) with an authentic sample.

(*b*) A solution of compound (III) (0·2 g) in aqueous sodium hydroxide (10%; 2 ml) was heated at 50—60° for 5 h and then acidified with concentrated hydrochloric acid (pH 1—2) to give *5-(o-aminophenylcarbamoyl)pyridazine-4-carboxylic acid* (VII) (0·15 g) which was purified as follows. A solution in concentrated hydrochloric acid was treated with charcoal and filtered; the compound was then reprecipitated

with aqueous ammonium hydroxide (pH 3) and dried *in vacuo* (KOH and P_2O_5). After melting at about 190°, * the compound resolidified at higher temperature and then remelted between 220 and 230° (decomp.) (Found: C, 55·6; H, 3·9; N, 21·5. $C_{12}H_{10}N_4O_3$ requires C, 55·8; H, 3·9; N, 21·7%).

5-(*Benzimidazol-2-yl*)*pyridazine-4-carboxylic Acid* (VIII). —(*a*) A suspension of compound (VII) (1 g) in methanol (200 ml) was refluxed for 16 h. The *acid* (VIII) (0·6 g) was separated by filtration as yellow needles; evaporation of the mother liquors left a residue which was treated with water, dried, and washed with hot chloroform to give a second crop (0·06 g, overall yield 71%) which darkened above 220° and melted at about 230° (decomp.) (after crystallisation from water) (Found: C, 60·2; H, 3·3; N, 23·1. $C_{12}H_8N_4O_2$ requires C, 60·0; H, 3·4; N, 23·3%); $\nu_{max.}$ 2500 and 1900br (NH^+), 1597 and 1375 cm^{-1} (CO_2^-) (NH absorption absent); $\lambda_{max.}$ 220sh, 240sh, and 331 nm (log ε 4·18, 3·96, and 4·09).

(*b*) Compound (XI) (1 g) was refluxed in aqueous sodium hydroxide (10%; 10 ml) until evolution of dimethylamine ceased (6—7 h). Acidification with concentrated hydrochloric acid (pH 1—2) precipitated a yellow solid (0·6 g, 66%), identical (m.p., i.r. and n.m.r. spectra) with material prepared in (*a*).

(*c*) The tetracyclic derivative (XII) (0·14 g) was refluxed in aqueous dioxan (2 : 1 v/v; 7 ml) for 4 h. The mixture was cooled and filtered to give compound (VIII) (0·12 g, 80%), identical (m.p., i.r. and n.m.r. spectra) with material obtained by method (*a*).

2-(*Pyridazin-4-yl*)*benzimidazole* (IX).—(*a*) A paste of pyridazine-4-carboxylic acid (X) [6] (0·35 g) and *o*-phenylenediamine (0·31 g) with polyphosphoric acid (83% P_2O_5; 3·5 g) was prepared at 50—60°. The mixture was heated at 200° for 5 h, cooled, treated with water (20 ml), and filtered; neutralisation of the filtrate with aqueous sodium hydroxide precipitated a solid which was sublimed at 195° and 0·02 mmHg to yield *compound* (IX) (0·42 g, 69·5%), m.p. 259—260° (from water) (Found: C, 67·2; H, 4·1; N, 28·5. $C_{11}H_8N_4$ requires C, 67·3; H, 4·1; N, 28·6%); $\lambda_{max.}$ 215sh, 242sh, and 313 nm (log ε 4·26, 3·90, and 4·31).

(*b*) Compound (VIII) (0·05 g) was sublimed at 210—215° and 0·02 mmHg to give a pale yellow product (0·036 g, 88%), identical (m.p., i.r. and n.m.r. spectra) with material prepared by method (*a*).

Reaction of Compound (III) *with Hexamethylphosphoric Triamide.*—A mixture of compound (III) (3 g) and hexamethylphosphoric triamide (30 ml) was heated at 210—215° for 20 min. Removal of the solvent under reduced pressure left a solid residue which was treated with water (20 ml), filtered, and extracted with boiling ethyl acetate (250 ml). On cooling, NN-*dimethyl*-5-(*benzimidazol-2-yl*)*pyridazine*-4-*carboxamide* (XI) (1·68 g) separated as yellow crystals, m.p. 209—210° † (after several crystallisations from ethyl acetate). Evaporation of the mother liquors at room temperature and pressure gave a solid (0·75 g) which largely consisted of compound (XI) (t.l.c.) (Found: C, 62·7; H, 4·9; N, 26·2. $C_{14}H_{13}N_5O$ requires C, 62·9; H, 4·9; N, 26·2%); $\lambda_{max.}$ 235sh and 333 nm (log ε 3·98 and 4·21).

Pyridazino[4′,5′:3,4]*pyrrolo*[1,2-a]*benzimidazol*-11-*one* (XII).—(*a*) A suspension of the acid (VIII) (0·5 g) in acetic anhydride (15 ml) was refluxed for 15 min to give a red-brown solution. On cooling, *compound* (XII) separated as yellow-brown crystals which were collected and washed with anhydrous ether (0·36 g, 80%). A sample obtained by sublimation at 150° and 0·03 mmHg and crystallisation from ethyl acetate, darkened above 240° and melted at 263—264° (decomp.) (Found: C, 64·9; H, 2·7; N, 25·4. $C_{12}H_6N_4O$ requires C, 64·9; H, 2·7; N, 25·2%); $\lambda_{max.}$ 232, 265, 271, 292, 302, and 365 nm (log ε 4·29, 4·37, 4·52, 3·83, 3·76, and 3·82).

(*b*) Compound (III) (0·3 g) was sublimed at 210° and 15—20 mmHg to yield a crude product which was extracted with methylene chloride (60 ml). Evaporation of the extract gave a yellow solid (0·1 g), identical (m.p., i.r. and n.m.r. spectra) with the product just described (after several crystallisations from ethyl acetate).

Methyl 5-(*Benzimidazol-2-yl*)*pyridazine-4-carboxylate* (XIII).—A suspension of compound (XII) (0·06 g) in methanol (20 ml) was refluxed for 30 min and set aside overnight. Removal of the solvent under reduced pressure afforded *compound* (XIII) (0·065 g, 95%), m.p. 170° (decomp.) (from benzene) (Found: C, 61·2; H, 4·0; N, 22·2. $C_{13}H_{10}N_4O_2$ requires C, 61·4; H, 4·0; N, 22·0%); $\nu_{max.}$ 3250br (NH) and 1730 cm^{-1} (CO_2Me); $\lambda_{max.}$ 240sh and 330 nm (log ε 3·94 and 4·05).

6,11-*Dihydro*-1,4-*dimethylpyridazino*[4,5-c][1,6]*benzodiazocine*-5,12-*dione* (XV).—Condensation of the ester (XIV) (1 g) with *o*-phenylenediamine (0·43 g) carried out essentially as described for compound (III) gave the *dione* (XV) (0·47 g, 44%), m.p. 236—237° (decomp.) (after two crystallisations from water) (Found: C, 62·7; H, 4·6; N, 21·1. $C_{14}H_{12}N_4O_2$ requires C, 62·7; H, 4·5; N, 20·9%); $\nu_{max.}$ 3260, 3060 (NH), 1690, and 1680 cm^{-1} (CO); $\lambda_{max.}$ 210 and 268 nm (log ε 4·48 and 3·62).

3,6-*Dimethyl*-5-(o-*aminophenylcarbamoyl*)*pyridazine*-4-*carboxylic Acid* (XVII).—*o*-Phenylenediamine (0·4 g) in anhydrous tetrahydrofuran (10 ml) was added dropwise to a solution of 3,6-dimethylpyridazine-4,5-dicarboxylic anhydride (XVI) [1d] (0·65 g) in the same solvent and the mixture was stirred at room temperature for 6 h. The yellow *product* (1·05 g, quantitative yield) was filtered off and purified by dissolution in concentrated hydrochloric acid, filtration, and reprecipitation with aqueous ammonium hydroxide (pH 3), m.p. 204—205° * (decomp.) (from water) (Found: C, 58·7; H, 5·0; N, 19·3. $C_{14}H_{14}N_4O_3$ requires C, 58·7; H, 4·9; N, 19·6%).

2-(3,6-*Dimethylpyridazin*-4-*yl*)*benzimidazole* (XVIII).—(*a*) A mixture of the anhydride (XVI) (0·7 g) and *o*-phenylenediamine (0·43 g) in glacial acetic acid (30 ml) was refluxed for 1 h. The yellow-brown residue left after removal of the solvent under reduced pressure was triturated with water and filtered to yield *compound* (XVIII) (0·75 g, 85%), which was purified by several crystallisations from water and dried in *vacuo* at 110°; m.p. 188—190° (Found: C, 69·6; H, 5·4; N, 24·9. $C_{13}H_{12}N_4$ requires C, 69·6; H, 5·4; N, 25·0%); $\lambda_{max.}$ 225sh and 310 nm (log ε 4·10 and 4·14).

(*b*) A mixture of compound (XIX) (0·17 g) and polyphosphoric acid (83% P_2O_5; 2 g) was heated at 150° for 4 h. After cooling, water (20 ml) was added and the resulting solution was neutralised with aqueous sodium hydrogen carbonate to give a solid (0·15 g), identical (m.p., i.r. and n.m.r. spectra) with the product obtained by method (*a*)

* The m.p. is sensitive to the rate of heating.

† If heating was slow, compound (XI) changed into another crystalline form between 200 and 205°, and then melted at 229—230°.

[6] W. J. Leanza, H. J. Becker, and E. F. Rogers, *J. Amer. Chem. Soc.*, 1953, **75**, 4086.

(after crystallisation from water and drying *in vacuo* at 110°).

N-(o-*Aminophenyl*)-3,6-*dimethylpyridazine*-4-*carboxamide* (XIX).—A suspension of compound (XVII) (0·3 g) in methanol (90 ml) was refluxed for 18 h. Removal of the solvent under reduced pressure left a solid residue which was treated with ether (15 ml) and filtered to give *compound* (XIX) (0·2 g), m.p. 213—214° (from ethyl acetate) (Found: C, 64·4; H, 6·0; N, 23·2. $C_{13}H_{14}N_4O$ requires C, 64·4; H, 5·8; N, 23·1%); $\nu_{max.}$ 3500—2500br (NH_2 and NH) and 1675 cm^{-1} (CO); $\lambda_{max.}$ 230sh, 260sh, and 295 nm (log ε 4·09, 3·72, and 3·56).

1,4-*Dimethylpyridazino*[4′,5′:3,4]*pyrrolo*[1,2-a]*benzimidazol*-11-*one* (XX).—(*a*) Sublimation of the acid (XVII) (0·2 g) at 175° and 0·02 mmHg afforded a yellow solid which was extracted with methylene chloride (20 ml). The solution was evaporated to dryness to give *compound* (XX) (0·075 g), which darkened above 240° and melted at 263—264° (decomp.) (after two crystallisations from ethyl acetate) (Found: C, 67·1; H, 3·9; N, 22·7. $C_{14}H_{10}N_4O$ requires C, 67·2; H, 4·0; N, 22·4%); $\nu_{max.}$ 1755 cm^{-1} (CO); $\lambda_{max.}$ (CH_2Cl_2) 230, 270, 277, 300, 313, and 364 nm (log ε 4·3, 4·41, 4·53, 3·64, 3·53, and 3·88).

(*b*) Compound (XV) (0·2 g) was sublimed at 195° and 15—20 mmHg to give a product which was extracted with methylene chloride (20 ml). Evaporation to dryness yielded compound (XX) (0·05 g), identical (m.p., i.r. and n.m.r. spectra) with material prepared as above (after two crystallisations from ethyl acetate).

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