# 1*H*-Pyrrolo[2,3-*b*]pyridines. Part III.[1] A Novel Synthetic Route from 1-Substituted 2-Aminopyrroles

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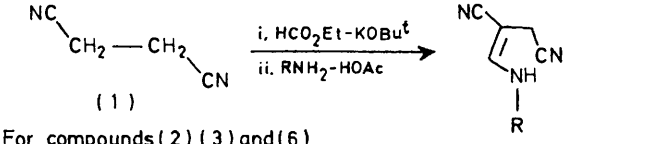
A variety of 1-alkyl- and 1-aryl-2-amino-4-cyanopyrroles have been shown to undergo condensation with 1,3-dicarbonyl compounds and their acetals, β-oxo-esters, and diethyl malonate in the presence of hydrochloric acid to yield, in one stage, 1*H*-pyrrolo[2,3-*b*]pyridines. With ethyl ethoxymethylenemalonate, 2-bis(ethoxycarbonyl)vinylaminopyrroles were isolated, and thermally cyclised to ethyl 4,7-dihydro-4-oxopyrrolo[2,3-*b*]pyridine-5-carboxylates. Spectroscopic evidence has been obtained for the structures of all the products.

PREVIOUS syntheses of 1*H*-pyrrolo[2,3-*b*]pyridines (4) have all involved the construction of the fused pyrrole ring on an appropriate pyridine. Many of the routes proved much more difficult than the indole preparations on which they were modelled.[2] We now report some syntheses of 1*H*-pyrrolo[2,3-*b*]pyridines from 2-aminopyrroles.



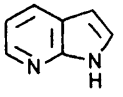

(1) (2)

For compounds (2), (3) and (6)

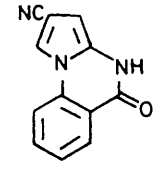
a; R = cyclohexyl
b; R = $PhCH_2$
c; R = $PhCH_2{\cdot}CH_2$
d; R = Ph
e; R = o-$MeC_6H_4$
f; R = m-$MeC_6H_4$
g; R = p-$MeC_6H_4$
h; R = o-$MeO{\cdot}C_6H_4$
i; R = m-$MeO{\cdot}C_6H_4$
j; R = p-$MeO{\cdot}C_6H_4$
k; R = o-$ClC_6H_4$
l; R = m-$ClC_6H_4$
m; R = p-$ClC_6H_4$
n; R = o-$MeO_2C{\cdot}C_6H_4$
o; R = m-$NO_2{\cdot}C_6H_4$
p; R = p-$NO_2{\cdot}C_6H_4$




(3)




(4)



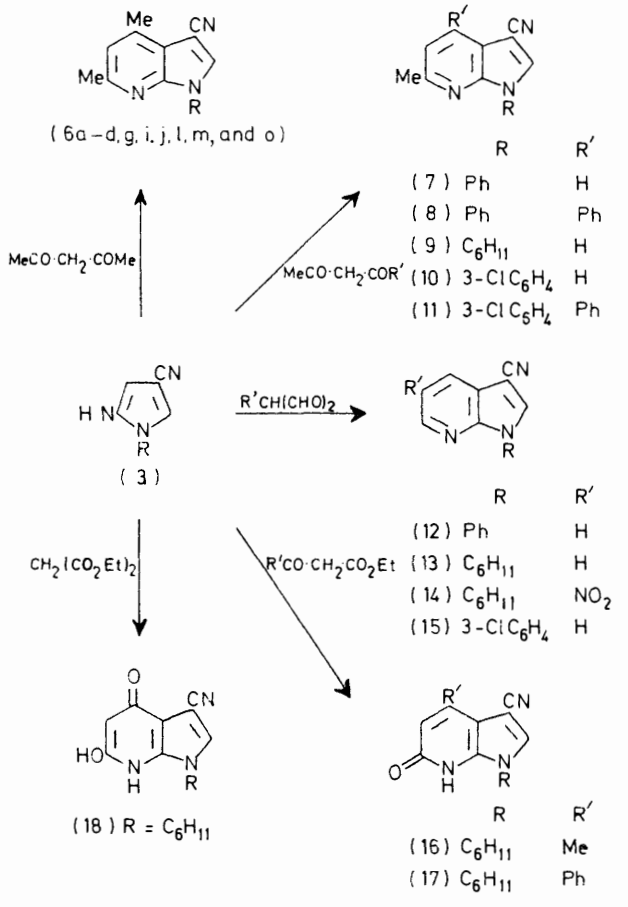

(5)

We first investigated the use of methyl 2-aminopyrrole-3-carboxylate[3] and the corresponding 3-carbonitrile.[4] These reactions proved unsuccessful and we therefore attempted to prepare, as starting materials, 2-aminopyrroles with a vacant 3-position. Simple 2-aminopyrroles are unstable but an electron-withdrawing group confers stability and the route to the 2-amino-4-cyanopyrroles from succinonitrile was adapted and extended.[5] This involves a three-step reaction in which succinonitrile (1) is condensed with ethyl formate and the potassium salt of the product is treated with an amine to yield an aminomethylenesuccinonitrile (2). Cyclisation of the latter, in the presence of potassium ethoxide, yields a 1-substituted 2-amino-4-cyanopyrrole (3). The $pK_a$ of the amine used (range 1.02—10.64) had no observable effect on the yield of either (2) or (3), but *o*-nitroaniline ($pK_a$ −0.3) did not react. The nitroanilinomethylene derivative (2o) gave a deep brown solution on treatment with potassium ethoxide but was cyclised satisfactorily on treatment with triethylamine under reflux for 3 h. The 2-methoxy-carbonyl derivative (2n) yielded not the corresponding pyrrole (3n) but the pyrrolo[1,2-*a*]quinazolone (5), which showed the long range *meta*-coupling ($J$ 2.0 Hz) typical of a 2,4-substituted pyrrole and no ester absorptions in its $^1$H n.m.r. spectrum. We then investigated the syntheses of pyrrolo[2,3-*b*]pyridines from a number of the 2-aminopyrroles by adaptation of methods previously used for the preparation of other bicyclic systems containing a similarly fused pyridine ring. Because there could be no ambiguity with respect to the structure of the products, we studied in most detail the reaction of pentane-2,4-dione with the aminocyanopyrroles to yield 4,6-dimethylpyrrolo[2,3-*b*]pyridine-3-carbonitriles (6). Uniformly high (50—80%) yields were obtained in ten different condensations effected in boiling ethanol in the presence of concentrated hydrochloric acid as catalyst. With unsymmetrical β-diketones, however, isomeric products are possible and condensation of 2-amino-4-cyano-1-cyclohexylpyrrole (3a) with 1-phenylbutane-1,3-dione yielded a product which had a sharp m.p. and a satisfactory analysis but which was shown by $^1$H and $^{13}$C n.m.r. spectroscopy to be a 40 : 60 mixture of 1-cyclohexyl-6-methyl-4-phenyl- and -4-methyl-6-phenyl-pyrrolo[2,3-*b*]pyridine-3-carbonitrile. From reactions of 2-amino-4-cyano-1-phenylpyrrole (3d) and 2-amino-1-(3-chlorophenyl)-4-cyanopyrrole (3l) with 1-phenylbutane-1,3-dione, however, only one isomer [(8) or (11)] was isolated, and in the closely related reactions of 4,4-dimethoxybutan-2-one with the two aminopyrroles (3a and l) in butan-1-ol the sole products were shown by $^1$H and $^{13}$C n.m.r. to be 6- [(9) and (10)] and not 4-methylpyrrolopyridines. Thus the $J_{4,5}$ value of 8.0 Hz was in the region expected for a pyridine ring bearing only H atoms in the 3- and 4-positions, and the $^{13}$C shift for the methyl group (24.5 p.p.m.) was in the range expected

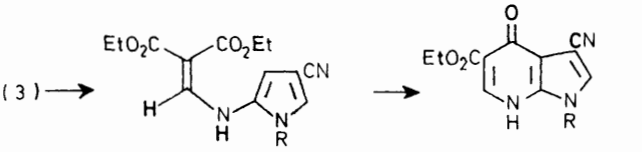
[1] Part II, R. Herbert and D. G. Wibberley, *J. Chem. Soc.* (*B*), 1970, 459.
[2] R. E. Willette, *Adv. Heterocyclic Chem.*, 1968, **9**, 27.
[3] T. D. Duffy and D. G. Wibberley, *J.C.S. Perkin I*, 1974, 1921.
[4] K. Gewald, *Z. Chem.*, 1961, **1**, 349.
[5] C. A. Grob and P. Ankli, *Helv. Chim. Acta*, 1950, **33**, 273, 658.

for an α-methylpyridine (*cf.* 2-methylpyridine, 24.2 p.p.m.).[6] This orientation depends on the attack of the aldehyde rather than the acetyl group at the aromatic ring; a similar preference is shown in syntheses of quinolines,[7] naphthyridines,[8] and pyrido[2,3-*d*]pyrimidines.[9]

Similar methods were used for the syntheses of the pyrrolo[2,3-*b*]pyridines bearing no substituent in the pyridine ring. In the case of the 1-cyclohexyl derivative (13), 1,1,1,3-tetramethoxypropane and the pyrrole (3a) were heated under reflux in ethanol with a little hydrochloric acid, whereas butanol was preferable for the phenyl derivative (12). Conditions previously used in the quinoline series[10] proved successful for the isolation of nitro(sodio)malonaldehyde and its condensation with the aminopyrrole (3a) in ethanol and acetic acid to yield the first reported pyrrolopyridine (14) to bear a nitro-substituent in the pyridine ring. A similar condensation of the pyrrole (3a) and ethyl acetoacetate in butan-1-ol in the presence of concentrated hydrochloric acid yielded 1-cyclohexyl-6,7-dihydro-4-methyl-6-oxopyrrolo[2,3-*b*]-pyridine-3-carbonitrile (16).

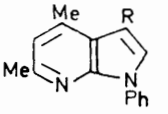



A two-stage thermally induced cyclisation in the absence of catalyst, previously used for the preparation of 1,8-naphthyridines,[11] was adapted for the synthesis of 1-cyclohexyl-6,7-dihydro-4-hydroxy-6-oxopyrrolo[2,3-*b*]pyridine-3-carbonitrile (18). First a mixture of the aminopyrrole (3a), diethyl malonate, and diphenyl ether




(19) R = $CH_2Ph$
(20) R = 4-$MeC_6H_4$
(21) R = $C_6H_{11}$
(22) R = 3-$ClC_6H_4$

(23) R = $CH_2Ph$
(24) R = 4-$MeC_6H_4$
(25) R = $C_6H_{11}$
(26) R = 3-$ClC_6H_4$



(27) R = $CO·NH_2$
(28) R = $CO_2H$

is heated at 140 °C until the initial evolution of ethanol has subsided, and then heating is continued under reflux.

The reaction of the aminopyrrole with ethoxymethylenemalonates and the cyclisation of the resulting 2-bisethoxycarbonylvinylaminopyrroles (19)—(22) by heating under reflux in diphenyl ether proved to be as useful a procedure for this, as in other, ring systems.[7-9] The intermediates showed the large (12 Hz) coupling constant, which disappears on deuteriation, typical of vinylamino-derivatives.[12] The pyrrolopyridin-4-ones (23)—(26) showed the expected NH (3100—3150) and ring C=O (1640—1680 $cm^{-1}$) absorptions in their i.r. spectra. One of the products (6d) from the pentanedione route was used in the study of the stability of the ring system to reaction conditions necessary to modify the substituents. Hydrolysis of the nitrile (6d) to an amide (27) required treatment with concentrated sulphuric acid at 100 °C for 4 h, and hydrolysis to the acid (28) took place with 15% sodium hydroxide under reflux for 15 h. The ring system remained unaffected under these conditions.

## EXPERIMENTAL

I.r. spectra were measured for Nujol mulls, with a Unicam SP 200 spectrometer. $^1H$ N.m.r. spectra were recorded with a Varian A-60A spectrometer (internal $Me_4Si$ standard) and $^{13}C$ n.m.r. spectra with a Varian HR 220 instrument operating at 22.63 MHz (internal $Me_4Si$ standard; positive shifts in p.p.m. downfield from $Me_4Si$). Mass spectra were recorded on an A.E.I. MS9 instrument operating at 70 eV. All analyses for new compounds were within accepted limits for C, H, and N and are recorded, together with i.r. and mass

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[7] R. C. Elderfield, 'Heterocyclic Compounds,' Wiley, New York, 1952, vol. IV, p. 1.
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[11] G. R. Lappin, Q. R. Peterson, and C. E. Wheeler, *J. Org. Chem.*, 1950, **15**, 377.
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spectroscopic data in Supplementary Publication No. SUP. 21456 (19 pp., 1 microfiche).†

*General Method for the Preparation of Aminomethylenesuccinonitriles* (2a—p).—The potassio-derivative of formylsuccinonitrile [4] (0.025 mol) dissolved in water (10 cm³) was treated with the appropriate amine (0.025 mol) followed by acetic acid (10 cm³), and the mixture was heated on a steam-bath for 10 min. An adequate yield of the almost pure *aminomethylenesuccinonitrile* separated on cooling and the product was crystallised (generally from ethanol).

*General Method for the Preparation of 2-Amino-4-cyanopyrroles* (3a—g, i, j, l, m, and o).—The aminomethylenesuccinonitrile (0.01 mol) was stirred at room temperature for 2 h in ethanolic potassium ethoxide [from potassium (0.025 mol) in ethanol (25 cm³)]. The ethanol was evaporated off and the residue triturated with water. On some occasions the *aminopyrrole* separated as a solid at this stage; otherwise the mixture was extracted with ether, the extract was washed with acid, the resultant acidic extract was basified, and the aminopyrrole was extracted into ether. Evaporation of this extract generally yielded the product as a solid, but three of the amines (3b—d) remained liquid and were purified by distillation. All the amines were converted into their *acetyl derivatives* for characterisation.

*4,5-Dihydro-5-oxopyrrolo*[1,2-a]*quinazoline-2-carbonitrile* (5).—Similar treatment of the aminomethylene derivative (2n) with potassium ethoxide gave a yellow solution from which the product began to separate within a few minutes. Work-up by the procedure for the aminopyrroles yielded the sparingly soluble *pyrroloquinazolone* (5) (95%), soluble in aqueous alkali, m.p. >300° (from dimethylformamide) (Found: C, 68.8; H, 3.5; N, 20.25%; $M^+$, 209.0590. $C_{12}H_7N_3O$ requires C, 68.9; H, 3.4; N, 20.1; *M*, 209.0589), $\lambda_{max.}$ (MeOH and MeOH–HCl) 263, 232, and 226 nm, $\lambda_{max.}$ (EtOH–NaOH) 294, 285, 268, and 259 nm, τ [$(CD_3)_2SO$; 100 °C; 100 MHz] 1.3 (1 H, s, 1-H), 1.4—2.2 (4 H, m, 6-, 7-, 8-, and 9-H), and 3.7 (1 H, s, 3-H) $\nu_{max.}$ 3100 (NH), 2250 (C≡N), and 1690 (C=O) $cm^{-1}$.

*General Method for the Preparation of 4,6-Dimethylpyrrolo*[2,3-b]*pyridine-3-carbonitriles* (6a—d, g, i, j, l, m, *and* o).—The aminopyrrole (3) (0.01 mol), pentane-2,4-dione (0.01 mol), ethanol (50 cm³), and concentrated hydrochloric acid (0.1 cm³) were heated under reflux for 4 h. The bulk of the ethanol was evaporated off and a little water was added until the *pyrrolo*[2,3-b]*pyridine* began to separate. The products were recrystallised (generally from ethanol). Analyses, m.p.s, and i.r. spectra are recorded in the Supplementary Publication.

*General Method for the Preparation of the Pyrrolo*[2,3-*b*]*pyridines* (7)—(17).—The aminopyrrole (0.01 mol) and the 1,3-dione or the corresponding acetal or the β-oxo-ester (0.01 mol) and concentrated hydrochloric acid (0.1 cm³) were heated together in either butanol or ethanol for the stated time. Products were isolated by an appropriate procedure of concentration or dilution and recrystallised from the stated solvent. Analyses and i.r. spectra are recorded in the Supplementary Publication. In this manner the aminopyrrole (3d) and 1-phenylbutane-1,3-dione (EtOH; 4 h) gave, after evaporation and dilution with water, the *pyrrolopyridine* (8) (65%), prisms (from aqueous ethanol), m.p. 171—172°, τ ($CF_3$·$CO_2H$) 2.25 (1 H, s, 2-H), 2.70 (1 H, s, 5-H), 2.8—3.0 (10 H, m, ArH), and 7.32 (3 H, s, 6-Me). The aminopyrrole (3l) and 1-phenylbutane-1,3-dione (EtOH; 4 h) gave, on cooling, the *pyrrolopyridine* (11) (61%), matted needles (from aqueous ethanol), m.p. 214—215°, τ ($CF_3$·$CO_2H$) 2.15 (1 H, s, 2-H), 2.65 (1 H, s, 5-H), 2.75—2.85br (9 H, s, ArH), and 7.30 (3 H, s, 6-Me). Similar treatment of 2-amino-4-cyano-1-cyclohexylpyrrole (3a) gave a product in 67% yield, as yellow prisms (from aqueous ethanol), m.p. 155—156°, which had satisfactory analytical figures but which was shown by its $^1H$ and $^{13}C$ n.m.r. spectra to be a mixture: τ ($CDCl_3$) 1.98 and 2.12 (1 H, s, 2-H), 2.25 and 2.30 (1 H, s, 5-H), 2.55br and 2.65br (5 H, s, Ph), 7.25 and 7.32 (3 H, s, $CH_3$), and 8.25—9.25 (11 H, m, cyclohexyl), $\delta_C$ 24.5 (2-$CH_3$) and 18.1 p.p.m. (4-$CH_3$) (*cf.*[5] 2-picoline, 24.2 p.p.m.; 4-picoline, 20.6). The aminopyrrole (3l) and 4,4-dimethoxybutan-2-one (BuOH; 2 h) were refluxed together. The solvent was evaporated off and the residue triturated with light petroleum to yield the pyrrolopyridine (10) (92%), needles (from ethanol), m.p. 174—175°, τ [$(CD_3)_2SO$] 1.50 (1 H, s, 2-H), 2.20 (4 H, m, $C_6H_4$), 2.70 (1 H, d, *J* 8 Hz, 4-H), and 2.95 (1 H, d, *J* 8 Hz, 5-H). The aminopyrrole (3a) and 4,4-dimethoxybutan-2-one (EtOH; 6 h) were heated under reflux. The solution was cooled and diluted with water to yield the *pyrrolopyridine* (9) (89%), yellow prisms [from light petroleum (b.p. 60—80°)], m.p. 137—138°, τ ($CDCl_3$) 2.27 (1 H, s, 2-H), 2.12 (1 H, d, *J* 8 Hz, 4-H), 2.92 (1 H, d, *J* 8 Hz, 5-H), 7.37 (3 H, s, 6-Me), and 7.70—8.60 (11 H, m, cyclohexyl). The aminopyrrole (3d) and 4,4-dimethoxybutan-2-one (EtOH; 6 h) similarly gave the *pyrrolopyridine* (7) (78%), matted needles [from light petroleum (b.p. 60—80°)], m.p. 153—154°, τ ($CF_3$·$CO_2H$) 1.60 (1 H, d, *J* 8 Hz, 4-H), 2.15 (1 H, s, 2-H), 2.60 (1 H, d, *J* 8 Hz, 5-H), 2.75 (5 H, m, Ph), and 7.36 (3 H, s, 6-Me). The aminopyrrole (3d) and 1,1,3,3-tetramethoxypropane (BuOH; 2 h) gave the *pyrrolopyridine* (12) (43%), prisms (from aqueous ethanol), m.p. 205—206°, τ ($CF_3$)($CO_2H$) 1.5 (1 H, m, 6-H), 1.85 (1 H, m, 4-H), 2.15 (1 H, s, 2-H), 2.5 (1 H, m, 5-H), and 2.9br (5 H, s, Ph). The aminopyrrole (3a) and 1,1,3,3-tetramethoxypropane (BuOH; 2 h), gave the *pyrrolopyridine* (13) (76%), needles [from light petroleum b.p. (60—80°)], m.p. 116—117°, τ ($CDCl_3$) 1.56 (1 H, q, $J_{5,6}$ 6, $J_{4,6}$ 1.2 Hz, 6-H), 1.92 (1 H, q, $J_{4,5}$ 8, $J_{4,6}$ 1.2 Hz, 4-H), 2.2 (1 H, s, 2-H), 2.81 (1 H, q, $J_{4,5}$ 8, $J_{5,6}$ 6 Hz, 5-H), and 7.6—8.6 (11 H, m, $C_6H_{11}$). The aminopyrrole (3l) and 1,1,3,3-tetramethoxypropane (BuOH; 3 h) gave the *pyrrolopyridine* (15) (92%), needles [from light petroleum b.p. (60—80°)], m.p. 223—224°, τ ($CF_3$·$CO_2H$) 1.4 (1 H, d, *J* 8 Hz, 6-H), 1.75 (1 H, d, *J* 6 Hz, 4-H), 2.05 (1 H, s, 2-H), 2.35 (1 H, m, 5-H), and 2.75 (4 H, m, $C_6H_4$). The aminopyrrole (3a) (1.89 g) and nitromalonaldehyde [liberated *in situ* from its sodio-derivatives (1.45 g) by addition of glacial acetic acid (5 cm³)] after treatment in the normal manner (4 h reflux) yielded, on cooling, the *nitropyrrolopyridine* (14), matted needles (from ethanol), m.p. 224—225°, τ ($CDCl_3$) 0.76 (1 H, d, *J* 1.2 Hz, 6-H), 1.16 (1 H, d, *J* 1.2 Hz, 4-H), 1.98 (1 H, s, 2-H), and 7.7—8.8 (11 H, m, $C_6H_{11}$). The aminopyrrole (3a) and ethyl acetoacetate in (BuON; 3 h) yielded after concentration by distillation, the *pyrrolopyridone* (16) (55%), microprisms (from chloroform), m.p. 283—284°, τ ($CF_3$·$CO_2H$) 2.0 (1 H, s, 2-H), 3.05 (1 H, s, 5-H), 7.1 (3 H, s, 4-Me), and 7.8—8.3 (11 H, m, $C_6H_{11}$). The aminopyrrole (3a) and ethyl benzoylacetate (BuOH; 2 h) yielded, after concentration by distillation, the *pyrrolopyridone* (17) (75.7%), microprisms (from ethanol), m.p. 313—314°.

*1-Cyclohexyl-6-hydroxy-4-oxo-7-pyrrolo*[2,3-b]*-pyridine-3-carbonitrile* (18).—The aminopyrrole (3a) (1.8 g) and diethyl malonate (1.7 g) were heated in diphenyl ether

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

(10 g) to 145 °C for 15 min, and then under reflux for 105 min. The mixture was cooled and diluted with light petroleum to yield the *pyrrolopyridone* (18) (83%), needles (from pyridine and then from dimethylformamide), m.p. 238—240° (decomp.), τ [$(CD_3)_2SO$] 2.02 (1 H, s, 2-H), 4.06 (1 H, s, 5-H), 5.4br (1 H, s, NH), and 7.9—8.9 (11 H, m, $C_6H_{11}$).

*Preparation of the* 2-(2,2-*Bisethoxycarbonylvinyl*)*amino-pyrroles* (19)—(22).—The aminopyrrole (0.01 mol) and diethyl ethoxymethylenemalonate (EMME) (0.11 mol) were heated together in butan-1-ol or ethanol for the stated time and the products were isolated by an appropriate method. Thus the aminopyrrole (3b) and EMME (BuOH; 3 h) gave, after concentration and trituration with light petroleum, the *vinylaminopyrrole* (19) (75%), needles (from aqueous ethanol), m.p. 110—112°, τ ($CDCl_3$) 2.1 (1 H, d, *J* 12 Hz, NH–CH=), 2.7br (5 H, s, Ph), 3.05 (1 H, d, *J* 2 Hz, 2-H), 3.85 (1 H, d, *J* 2 Hz, 4-H), 5.0 (2 H, s, $CH_2Ph$), 5.9 (4 H, q, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$), and 8.82 (6 H, t, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$). The aminopyrrole (3 g) and EMME (BuOH; 1.5 h) gave, on concentration, the *vinylaminopyrrole* (20) (90%), prisms (from carbon tetrachloride), m.p. 153—154°, τ ($CDCl_3$) −0.55br (1 H, removed on deuteriation, NH), 1.95 (1 H, d, *J* 13 Hz; s on deuteriation, NH–C*H*=), 2.70 (4 H, ABq, $C_6H_4$), 2.90 (1 H, d, *J* 2 Hz, 2-H), 3.75 (1 H, d, *J* 2 Hz, 4-H), 5.50 (4 H, q, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$), 7.55 (3 H, 2, $CH_3$), and 8.7 (6 H, t, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$). The aminopyrrole (3a) and EMME (EtOH; 14 h) gave, after concentration and trituration with light petroleum, the *vinylaminopyrrole* (21) (80%), needles (from aqueous ethanol), m.p. 131—132°, τ ($CDCl_3$) 2.0 (1 H, d, *J* 12 Hz, NH–C*H*=), 3.0 (1 H, d, *J* 2 Hz, 2-H), 3.9 (1 H, d, *J* 2 Hz, 4-H), 5.85 (4 H, q, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$), 7.9—8.6 (11 H, m, $C_6H_{11}$), and 8.75 (6 H, t, *J* 7 Hz, 2 × $CH_2{\cdot}CH_3$). The aminopyrrole (3l) and EMME (EtOH; 6 H) gave, on concentration, the *vinylaminopyrrole* (22) (91%), needles [from light petroleum (b.p. 60—80°)], m.p. 155—157°, τ ($CDCl_3$) —0.75br (1 H, removed by deuteriation, NH), 1.95 (1 H, d, *J* 13 Hz; s on deuteriation, NH–C*H*=), 2.65 (4 H, m, $C_6H_4$), 2.80 (1 H, d, *J* 2 Hz, 2-H), 3.65 (1 H, d, *J* 2 Hz, 4-H), 5.8 (4 H, q, *J* 6.5 Hz, 2 × $CH_2{\cdot}CH_3$), and 8.7 (6 H, t, *J* 6.5 Hz, 2 × $CH_2{\cdot}CH_3$).

*Preparation of the Pyrrolo*[2,3-b]*pyridin*-4(7H)-*ones* (23)—(26).—The 2-(2,2-bisethoxycarbonyvinyl)aminopyrrole (19)—(22) (1 g) was heated in diphenyl ether (25 g) for 20 min at 250 °C. The solution was cooled and diluted with light petroleum (b.p. 60—80°) to yield the pyrrolo[2,3-*b*]pyridin-4(7*H*)-one. In this manner the vinylaminopyrrole (19) yielded the *pyrrolopyridine* (23) (63%), matted needles (from aqueous ethanol), m.p. 307—308°, τ ($CF_3{\cdot}CO_2H$) 0.95 (1 H, s, 6-H), 2.1 (1 H, s, 2-H), 2.65 (5 H, m, Ph), 4.34 (2 H, s, $CH_2$), 5.25 (2 H, q, *J* 8 Hz, $CH_2{\cdot}CH_3$), and 8.44 (3 H, t, *J* 8 Hz, $CH_2{\cdot}CH_3$). The vinylaminopyrrole (20) yielded the *pyrrolopyridone* (24) (74%), needles (from acetone), m.p. 234–235°, τ [$(CD_3)_2SO$; 40 °C] 1.42 (1 H, s, 6-H), 1.7 (1 H, s, 2-H), 2.68 (4 H, ABq, $C_6H_4$), 5.65 (2 H, q, *J* 6.5 Hz, $CH_2{\cdot}CH_3$), 7.5 (3 H, s, $CH_3$), and 8.75 (3 H, t, *J* 6.5 Hz, $CH_2{\cdot}CH_3$). The vinylaminopyrrole (21) yielded the *pyrrolopyridone* (25) (68%), needles [from chloroform–ethanol (1 : 10)], m.p. 220—221°, insufficiently soluble for n.m.r. spectrum. The vinylaminopyrrole (22) yielded the *pyrrolo-pyridone* (26) (61%), needles (from aqueous acetone), m.p. 205—206°, insufficiently soluble for n.m.r. spectrum.

4,6-*Dimethyl*-1-*phenylpyrrolo*[2,3-b]*pyridine*-3-*carboxamide* (27).—The pyrrolopyridinecarbonitrile (6d), concentrated sulphuric acid (5 $cm^3$), and water (0.5 $cm^3$) were heated together at 100 °C for 4 h. The solution was poured onto crushed ice and basified with 10% sodium hydroxide to yield the *carboxamide* (27), prisms [from chloroform–carbon tetrachloride (1 : 1)], m.p. 234—235° (Found: C, 72.3; H, 5.7; N, 15.7. $C_{16}H_{15}N_3O$ requires C, 72.4; H, 5.7; N, 15.8%), $\nu_{max.}$ (Nujol) 3405 and 3215 ($NH_2$), and 1640 $cm^{-1}$ (C=O).

4,6-*Dimethyl*-1-*phenylpyrrolo*[2,3-b]*pyridine*-3-*carboxylic Acid* (28).—The pyrrolopyridinecarbonitrile (6d) was dissolved in ethanol (25 $cm^3$), a solution of sodium hydroxide (2.5 g) in water (25 $cm^3$) was added, and the mixture was heated at 100 °C for 15 h, concentrated, and acidified to yield the *acid* (28), microprisms (from aqueous ethanol), m.p. 233—234° (decomp.) (Found: C, 72.0; H, 5.3; N, 10.0%; $M^+$, 266.1052. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%; *M*, 266.1055), $\nu_{max.}$ (Nujol) 2800—2600 (OH) and 1690 $cm^{-1}$ (C=O).

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