The Elimination of an Alkoxy Group in the Photo-Graebe–Ullmann Conversion of 1-(2,5-Dialkoxyphenyl)triazolopyridines into Carbolines, and the Preparation of α-, γ- and δ-Carboline Quinones

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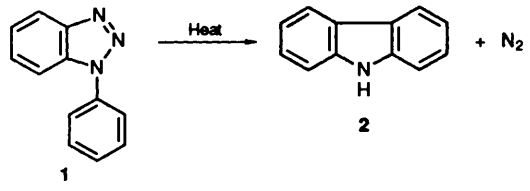
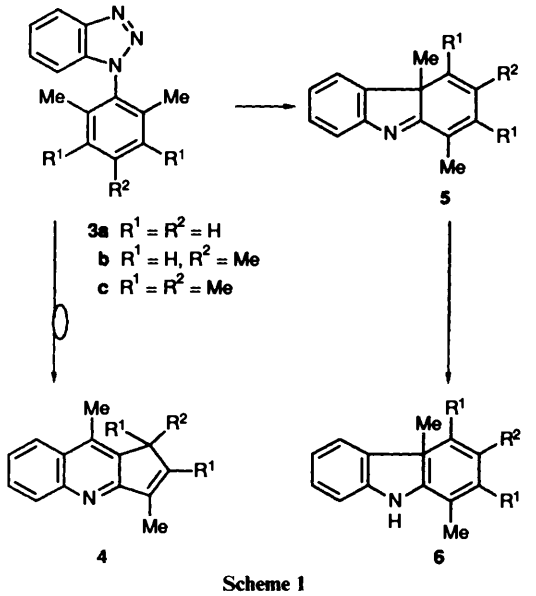
Photochemical decomposition of 1-(2,5-dialkoxyphenyl)triazolopyridines **7a**, **21** and **33** resulted in elimination of an alkoxy group to give the alkoxycarbolines **9a** and **35** in addition to the expected dialkoxycarbolines. The carbolines having either a methoxy and a isopropoxy substituent **22**, **34a** and **34b** or two methoxy groups **41** were oxidised with ceric ammonium nitrate to yield the α-, γ- or δ-carboline *p*-quinones **37**, **38** and **42**.

The thermal decomposition of 1-phenylbenzotriazole **1** to give the carbazole **2** (the Graebe–Ullmann reaction) was observed



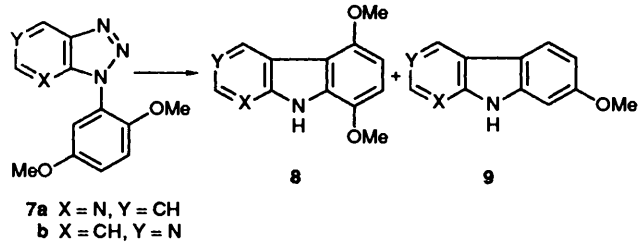
nearly a century ago.[1] The photodecomposition of benzotriazoles also gives carbazoles[2] and sometimes provides compounds not accessible by the thermal route.[3] Both the thermal- and the photo-reactions of 1-phenylbenzotriazole carrying a methyl group at each of the *ortho* positions of the phenyl group have been studied.[4] For the immediate purposes here it is sufficient to note that photocyclisation of **3** produced a rearranged major product **4** (Scheme 1). In the case of **3a** but



Scheme 1

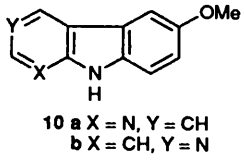
more particularly for **3b** and **3c**, where there is more crowding of substituents on the phenyl group, the carbazoles, **6a–c**, are also formed by loss of a methyl group from the 4a*H*-carbazoles **5a–c**, respectively.[4]

In later work designed to produce carboline quinones having a *p*-quinonoid system, we sought to prepare dimethoxycarbolines as precursors of the quinones. The dimethoxycarbolines were prepared by application of the photo-Graebe–Ullmann reaction to *N*-(2,5-dimethoxyphenyl)triazolopyridine.[5] Photo-decomposition of each of the triazolopyridines **7a** and **7b** (Scheme 2) gave the expected dimethoxycarbolines **8a**



Scheme 2

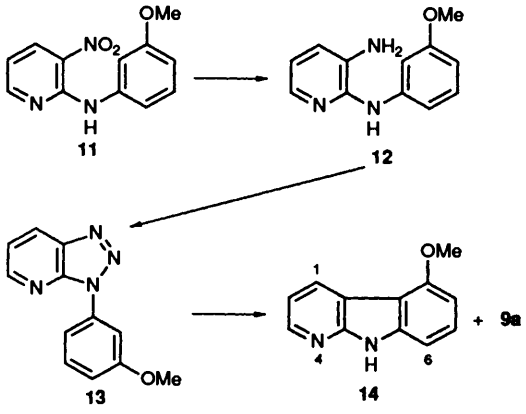
and **8b** but, in addition, demethoxylated compounds **9a** and **9b**, respectively, were isolated as minor products. In these examples, the alkoxy substituents on the phenyl group were not crowded. The structures **9a** and **9b** were deduced from their method of formation and from ^{1}H NMR evidence but the small possibility remained that they were the isomeric **10a** and **10b**



because isomers such as **9a** and **10a** are difficult to distinguish by NMR spectroscopy. We therefore decided to synthesise **9a** unambiguously.

3-(3-Methoxyphenyl)triazolo[4,5-*b*]pyridine **13** was readily obtained from *m*-anisidine and 2-chloro-3-nitropyridine *via* the isolated intermediate nitro amine **11** (Scheme 3) and its reduction to the diamine **12**. Diazotisation of this diamine gave the triazolopyridine **13** in high yield and this, on photochemical decomposition, efficiently gave two products. The first product isolated by chromatography was the novel 9-methoxy-α-carboline **14** and the second was 7-methoxy-α-carboline **9a**, identical with the compound formed in the photo-Graebe–Ullmann reaction of the 3-(dimethoxyphenyl)benzotriazole **7a**,[5] thus confirming the identity of this unexpected product.

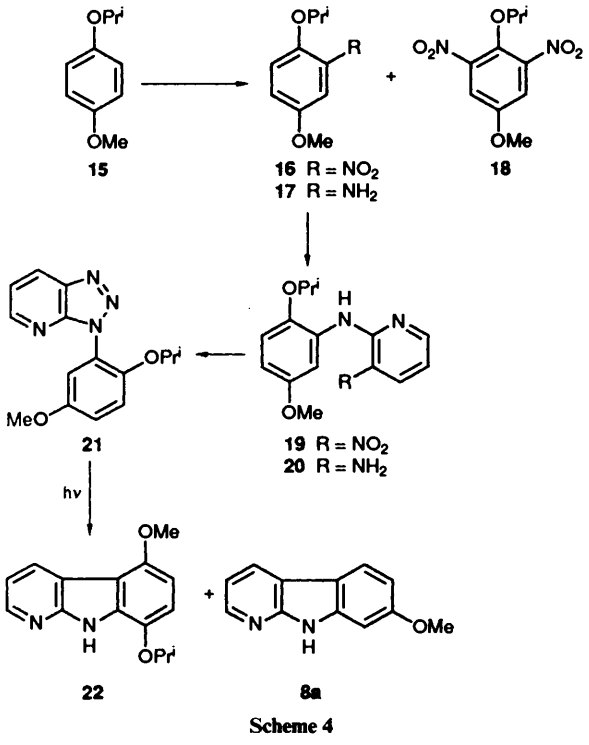
Our objective was to prepare the carboline *p*-quinones from the corresponding dialkoxy compounds and, therefore, it was desirable to limit the extent of the process leading to the formation of the monoalkoxy compound. We reasoned that an increase in the steric size of the alkoxy group, which becomes the bridgehead alkoxy substituent in the undesirable reaction



Scheme 3

pathway, might lead to an increased yield of the required dialkoxy compounds. We chose to study the reactions of 1-(2,5-dialkoxyphenyl)triazolopyridines, where the alkoxy groups were different, *viz* methoxy and isopropoxy.

The nitration of *p*-isopropoxyanisole **15** by the Goldworthy procedure[6] gave several products (TLC), but column chromatography yielded 4-isopropoxy-3-nitroanisole **16**, pure by TLC, and 3,5-dinitro-4-isopropoxyanisole **18** (Scheme 4). Reduction

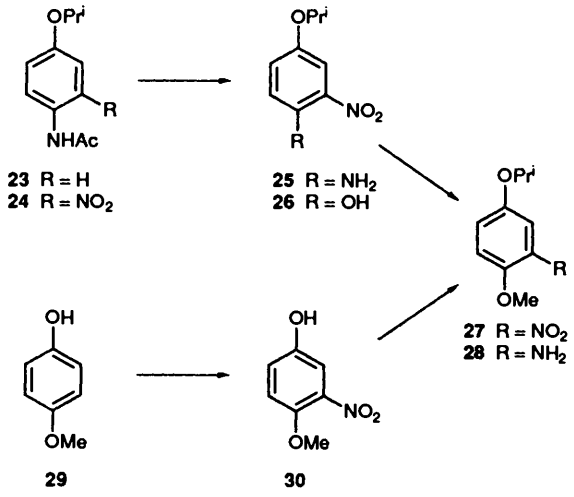


Scheme 4

of **16** to the dialkoxyaniline **17** and its reaction with 2-chloro-3-nitropyridine gave the secondary amine **19**.

Hydrogenation of the nitro group of **19** and diazotisation of the resulting amine **20** proceeded normally to give the required triazole **21**. Photolysis of the triazole **21** gave a mixture containing 6-isopropoxy-9-methoxy-α-carboline **22** in high yield (84%) and 7-methoxy-α-carboline **9a** (9%). This showed an improved overall yield and a higher proportion of the dialkoxycarboline compared with the results obtained in the photolysis of 1-(2,5-dimethoxyphenyl)triazolopyridine **7a**.[5] Thus it appeared that an increased yield of carboline was obtained when the 2-alkoxy substituent in the triazole was more sterically demanding.

We made a similar comparison of the photolysis of the

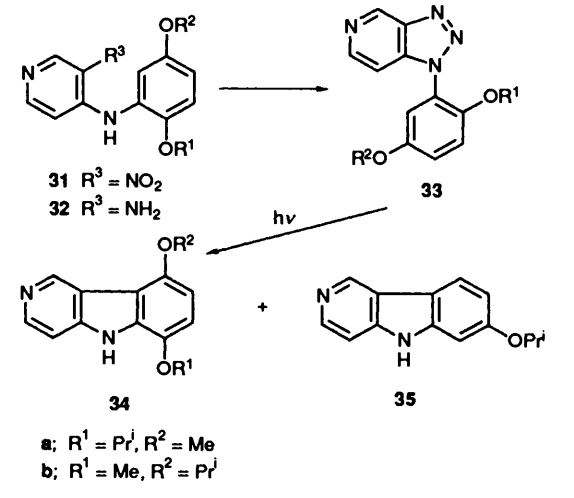


Scheme 5

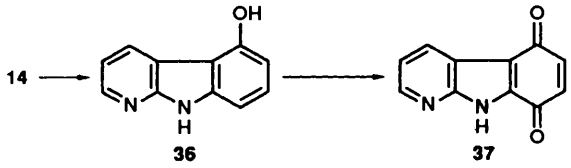
isomeric 1-(dialkoxyphenyl)triazolo[4,5-*c*]pyridines **33a** and **33b** leading to the γ-carbolines **34a** and **34b** (Scheme 6). In the case of **34a** an isopropoxy group is expected to be a substituent at the bridgehead of the intermediate while in the case of **34b** the less sterically demanding methoxy group is the corresponding substituent. In order to be able to prepare **34b**, the unknown 4-isopropoxy-2-nitroanisole **27** was required. Our first approach was a five-step route (Scheme 5) from commercially available 4-hydroxyacetanilide through the known isopropoxy ether **23**, followed by nitration to give **24**, and deacetylation to give **25**.

The phenol **27** was first obtained in very low yield from **26** by the action of aqueous alkali following the procedure reported[7] for the preparation of 4-methoxy-2-nitrophenol from the corresponding aniline. The ether **27** was then obtained from **26**. Later we used a much better route of four steps from 4-hydroxyanisole **29** involving etherification of the known phenol **30**. Reduction of **27** gave the amine **28**. The separate reaction of the isomeric aminoisopropoxyanisoles **17** and **28** with 4-chloro-3-nitropyridine gave the isomeric nitroamines **31a** and **31b**, which were reduced to the diamines **32a** and **32b**, and then converted into the triazolo[4,5-*c*]pyridines **33a** and **33b**, respectively.

Photolysis of **33a** gave a mixture from which only the γ-carboline (pyrido[4,3-*b*]indole) **34a** was isolated in poor yield (36%). The isomeric triazolopyridine **33b** also gave a mixture on photolysis and an even lower yield (30%) of the expected



Scheme 6

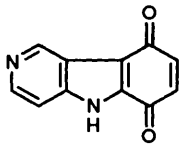


Scheme 7

dialkoxy-γ-carboline **34b** was obtained. However, in this case, 7-isopropoxy-γ-carboline **35** was isolated in 15% yield. It seemed likely that the photo-Graebe–Ullmann reaction was more efficient in causing the formation of α-carbolines than γ-carbolines but, since the yields were low, these results may reflect the problems encountered in the isolation of the products.

We now turned our attention to the preparation of the carboline quinones. The oxidation of the dimethoxy-α-carboline **8a** to the quinone **37** (47%) by ceric ammonium nitrate (CAN)[5] contrasts with the lack of success obtained when attempts were made to oxidise 1,4-dimethoxycarbazole[5] and 4,7-dimethoxyindole[8] with CAN. Now, the 6-isopropoxy-9-methoxy-α-carboline **22** gave the α-carboline quinone **37** smoothly by oxidation with CAN and in a good yield (83%). This may be due to greater stabilisation of the oxonium ion radical intermediate in the oxidation by the isopropyl group in **22** compared to that caused by the methyl group in **8a**. An alternative route to the quinone **37** (Scheme 7) from 9-methoxy-α-carboline **14** required the formation of the hydroxy compound **36** and its subsequent oxidation with Fremy's salt. The yield of the quinone **37** was 57% but attempted oxidations with silver carbonate or benzeneselenic anhydride were unsuccessful.

Three attempts were made to obtain the γ-carboline quinone **38**. The action of CAN on **8b** gave a stable but unidentified



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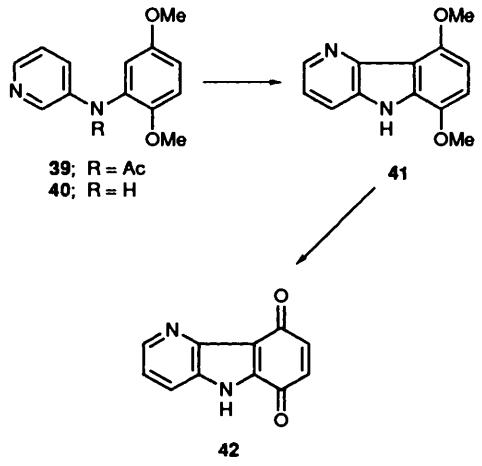
cream solid. However, the oxidation of **34a** and **34b** by CAN proceeded smoothly to give the quinone **38** in 50 and 32% yield, respectively. Thus, on the limited evidence available, it seems that the mixed alkoxides are better precursors for those quinones where CAN is an oxidising agent than the dimethoxy analogues.

In an attempt to provide routes to β- and δ-carbolines (pyrido[3,4-*b*]indoles and pyrido[3,2-*b*]indoles, respectively), we prepared 3-(2,5-dimethoxyanilino)pyridine **40** (Scheme 8) from 2,5-dimethoxyacetanilide and 3-bromopyridine in the presence of activated copper bronze and potassium carbonate by the Goldberg procedure[9] to give **39**, and then removed the acetyl group by hydrolysis. Photocyclisation of the secondary amine **40** gave the δ-carboline **41**. Oxidation of **41** with CAN gave the red quinone **42** in 58% yield. Attempts to prepare a substituted β-carboline by the method of Becalski *et al.*[10] for subsequent oxidation to the quinone were unsuccessful.



Scheme 8

Experimental

M.p.s were determined on an Electrothermal Digital apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1420 spectrometer and the NMR spectra on either a Varian CFT-20 or JEOL FX-200 spectrometer with tetramethylsilane as the internal standard. *J* values are given in Hz. Low resolution electron impact mass spectra were produced on an A.E.I. MS-902 spectrometer and the accurate mass measurements were provided by the SERC Mass Spectrometry Service, Swansea. Elemental analysis data were provided by Medac Ltd., Brunel University.

Analytical and preparative layer chromatography was carried out on 250 μm and 1 mm thick layers of silica gel 60A, respectively. A chromatotron (T.C. Research, St. Albans, UK) was used for radially accelerated layer chromatography on Merck 7749 silica gel. Column chromatography was performed on (May and Baker) silica gel 60 (40–60 μm) with the solvents under positive pressure. The solvents were distilled before use and light petroleum refers to the fraction with b.p. 40–60 °C. Photochemical reactions were carried out in a 1 dm^3 Hanovia reactor using a medium-pressure mercury lamp (125 W). 2-Chloro-3-nitropyridine was obtained from Aldrich Chemicals Co. and 4-chloro-3-nitropyridine was obtained by a literature procedure.[11]

4-Isopropoxy-3-nitroanisole **16**.—A mixture of conc. nitric acid (*d* 1.42; 9.3 g) and glacial acetic acid (36 cm^3) was added to a stirred mixture of 4-isopropoxyanisole[6] (16.8 g) in glacial acetic acid (18 cm^3) and propionic acid (6 cm^3) at 0 °C. The mixture was set aside at 0 °C for 10 min after which additional conc. nitric acid (4.6 g) was added with stirring. After 15 min the reaction mixture was poured into ice–water and extracted with chloroform. On evaporation the extract yielded a yellow oil which was separated into two major components by flash chromatography (light petroleum–ethyl acetate, 9:1). The major component [TLC: light petroleum–ethyl acetate (7:3), R_f 0.53] was the *title compound* obtained as a yellow oil (15.4 g, 72%), b.p. 80–82 °C at 0.8 mmHg; ν_{max}/cm^{-1} (liq.) 1530 and 1350 (NO_2); $\delta_H(CDCl_3)$ 1.33 (6 H, d, *J* 6, 2 × CH_3), 3.78 (3 H, s, OCH_3), 4.49 (1 H, heptet, *J* 6, CH), 7.0 (2 H, d, *J* 2, 5- and 6-H) and 7.25 (1 H, m, 2-H); *m/z* (%) 211 (8, M^+), 169 ($M^+ - C_3H_7$, 100), 152 (7), 123 (10), 111 (9) and 79 (5) (Found: C, 56.9; H, 6.3; N, 6.6. $C_{10}H_{13}NO_4$ requires C, 56.9; H, 6.2; N, 6.6%). Analysis by GLC (3% OV17 on Diatomite, 170 °C, FID) showed one component.

The second component, an orange solid crystallised from diisopropyl ether, was 4-isopropoxy-3,5-dinitroanisole (0.8 g, 4%), m.p. 102–103 °C (lit.,[6] m.p. 100–101 °C).

2-Isopropoxy-5-methoxyaniline **17**.—A mixture of the anisole **16** (12.83 g), palladium on charcoal (1.2 g, 10%) and methanol (200 cm^3) was shaken under an atmosphere of hydrogen (1 atm) at 26 °C for 5 h after which the solid was filtered off. On evaporation the filtrate yielded a brown oil which was distilled to give the colourless *title compound* (10.44 g, 94%), b.p. 66–68 °C at 0.8 mmHg; ν_{max}/cm^{-1} (liq.) 3460 and 3360 (NH_2);

$\delta_H(CDCl_3)$ 1.30 (6 H, d, *J* 6, 2 × CH_3), 3.62 (2 H, s, exchanged with D_2O, NH_2), 3.69 (3 H, s, OCH_3), 4.33 (1 H, heptet, *J* 6, CH), 6.20 (2 H, m, 3- and 4-H) and 6.68 (1 H, d, *J* 9, 6-H); *m/z* (%) 181 (M^+, 40), 139 (M^+ − 137, 100), 138 (71), 124 (37), 110 (32) and 96 (21) (Found: C, 66.15; H, 8.5; N, 7.6. $C_{10}H_{15}NO_2$ requires C, 66.3; H, 8.3; N, 7.7%).

4-Isopropoxy-2-nitroacetanilide **24**.—A stirred mixture of 4-isopropoxyacetanilide[12] (1 g), glacial acetic acid (1.6 cm^3) and nitric acid [prepared from conc. nitric acid (*d* 1.42; 1.12 cm^3) and water 6.15 cm^3] was stored for 24 h and then poured into ice–water. The solid was filtered off and purified by chromatography (light petroleum–ethyl acetate, 9:1) to give the *title compound* **24** (0.6 g, 50%), m.p. 79–80 °C (ex. aqueous ethanol); ν_{max}/cm^{-1} (KBr) 3360 (NH), 1680 (CO) and 1590 and 1380 (NO_2); $\delta_H[(CD_3)_2CO]$ 1.33 (6 H, d, *J* 6, 2 × CH_3), 2.16 (3 H, s, OCH_3), 4.69 (1 H, heptet, *J* 6, CH), 7.27 (1 H, dd, *J* 9 and 3, 5-H), 7.53 (1 H, d, *J* 3, 3-H), 8.17 (1 H, d, *J* 9, 6-H) and 9.61 (1 H, s, exchanged with D_2O, NH); *m/z* (%) 238 (M^+, 8), 154 (100), 148 (42), 147 (22) and 108 (29) (Found: C, 55.6; H, 6.0; N, 11.6. $C_{11}H_{14}N_2O_4$ requires C, 55.5; H, 5.9; N, 11.8%).

4-Isopropoxy-2-nitroaniline **25**.—Aqueous methanolic potassium hydroxide (1.3 cm^3) [made by dissolving potassium hydroxide (8.8 g) in water (6.3 cm^3) and diluting the solution with methanol (20 cm^3)] was added to the acetanilide **24** (0.9 g) and the mixture warmed on a steam-bath for 15 min. The mixture became a viscous red paste which, after the addition of hot water (1.3 cm^3), was stirred and heated on a steam-bath for a further 15 min. The cooled mixture (0–5 °C) yielded a solid which was recrystallised from aqueous ethanol to yield the *title compound* **25** (0.59 g, 80%), m.p. 58–59 °C; ν_{max}/cm^{-1} (KBr) 3500 (NH_2), 3480 (NH_2) and 1590 and 1350 (NO_2); $\delta_H(CDCl_3)$ 1.30 (6 H, d, *J* 6, 2 × CH_3), 4.42 (1 H, heptet, *J* 6, CH), 5.77 (2 H, s, exchanged with D_2O, NH_2), 6.68 (1 H, d, *J* 9, 6-H), 6.99 (1 H, dd, *J* 2, 5-H) and 7.52 (1 H, d, *J* 3, 3-H); *m/z* (%) 196 (M^+, 23), 154 (100) and 108 (71) (Found: C, 54.9; H, 6.15; N, 14.2. $C_9H_{10}N_2O_3$ requires C, 55.1; H, 6.2; N, 14.3%).

4-Isopropoxy-2-nitrophenol **26**.—A mixture of the aniline **25** (0.49 g), potassium hydroxide (0.28 g) and water (4.5 cm^3) was heated at reflux for 9 h and then allowed to cool. The solid was filtered off and the filtrate acidified with conc. hydrochloric acid to give a yellow solid which, recrystallised from aqueous ethanol, gave the *phenol* **26** (0.04 g, 8%), m.p. 42–44 °C; ν_{max}/cm^{-1} (KBr) 3520–3280 (OH) and 1545 and 1340 (NO_2); $\delta_H(CDCl_3)$ 1.33 (6 H, d, *J* 5, 2 × CH_3), 4.50 (1 H, heptet, *J* 6, CH), 7.07 (1 H, d, *J* 10, 6-H), 7.19 (1 H, dd, *J* 9 and 3, 5-H), 7.52 (1 H, d, *J* 2, 3-H) and 10.31 (1 H, s, exchanged with D_2O, OH); *m/z* (%) 197 (M^+, 7), 155 (56), 154 (19) and 149 (100) (Found: M^+, 197.0688; $C_9H_{11}NO_4$ *M*, requires 197.0688).

4-Isopropoxy-2-nitroanisole **27**.—

Method A. A mixture of the phenol **26** (0.03 g), potassium carbonate (0.02 g), methyl iodide (0.68 g) and dry acetone (10 cm^3) was heated at reflux for 3 h. The solid was then removed and the acetone evaporated to give a residue which, purified by column chromatography (ethyl acetate–light petroleum, 1:9), gave the *title compound* **27** (0.01 g, 30%) as an oil which was distilled (bulb-to-bulb), b.p. 48 °C (bath) at 1 mmHg; ν_{max}/cm^{-1} (liq.) 1550 and 1370 (NO_2); $\delta_H(CDCl_3)$ 1.33 (6 H, d, *J* 6, 2 × CH_3), 3.92 (3 H, s, OCH_3), 4.48 (1 H, heptet, *J* 6, CH), 7.01 (1 H, d, *J* 9, 6-H), 7.09 (1 H, dd, *J* 9 and 3, 5-H) and 7.39 (1 H, d, *J* 3, 3-H); *m/z* (%) 211 (M^+, 22), 160 (100) and 109 (38) (Found: C, 56.9; H, 6.25; N, 6.6. $C_{10}H_{13}NO_4$ requires C, 56.9; H, 6.2; N, 6.6%).

Method B. 4-Methoxy-3-nitrophenol **30**[13] (9.53 g) was allowed to react with 2-iodopropane (68.1 g) in a similar way to that described in method A. The oil was distilled to give a product (7.49 g, 63%), identical with that previously obtained.

Preparation of the Substituted Anilino-3-nitropyridines **11**, **19**, **31a** *and* **31b**. *General Method*.—A mixture of the appropriate chloronitropyridine, the alkoxy- or di-alkoxyaniline (1.2 mol equiv.), anhydrous sodium acetate (5 mol equiv.) and glacial acetic acid (*ca.* 5 cm^3 per gram of the aniline) was refluxed until the reaction was complete (TLC; 1–3 h). The mixture was poured into ice–water and either the solid filtered off or the mixture extracted with chloroform and the solvent evaporated.

2-(3-Methoxyanilino)-3-nitropyridine **11**, obtained from the chloroform extract, was purified by flash chromatography (ethyl acetate–light petroleum, 1:9). Crystallisation of the crude product from light petroleum gave the orange nitropyridine (79%), m.p. 98–99 °C (lit.,[14] m.p. 98–100 °C).

2-(2-Isopropoxy-5-methoxyanilino)-3-nitropyridine **19**. This compound, a solid, was crystallised from light petroleum to give dark red needles of the *anilinonitropyridine* **19** (59%), m.p. 121–122 °C; ν_{max}/cm^{-1} (KBr) 3440 (NH); $\delta_H(CDCl_3)$ 1.42 (6 H, d, 2 × CH_3), 3.82 (3 H, s, OCH_3), 4.55 (1 H, heptet, *J* 6, CH), 6.58 (1 H, dd, *J* 6 and 2, 4′-H), 6.84 (2 H, m, 3′- and 5-H), 8.44 (1 H, d, *J* 2, 6′-H), 8.55 (2 H, m, 4- and 6-H) and 10.95 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 303 (M^+, 45), 261 (M^+ − C_3H_7, 48), 245 (16), 244 (100) and 214 (41) (Found: C, 59.6; H, 5.5; N, 13.8. $C_{13}H_{17}N_3O_4$ requires C, 59.4; H, 5.6; N, 13.8%).

4-(2-Isopropoxy-5-methoxyanilino)-3-nitropyridine **31a**. This compound, a red oil, was distilled to give the *title compound* **31a** (72%), b.p. 96–98 °C at 0.8 mmHg; ν_{max}/cm^{-1} (liq.) 3340 (NH), 1550 and 1350 (NO_2); $\delta_H(CDCl_3)$ 1.29 (6 H, d, *J* 6, 2 × CH_3), 3.79 (3 H, s, OCH_3), 4.43 (1 H, heptet, *J* 6, CH), 6.77 (3 H, m, 3′-, 4′- and 6′-H), 7.12 (1 H, d, *J* 7, 5-H), 8.28 (1 H, d, *J* 7, 6-H), 9.28 (1 H, s, 2-H) and 9.75 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 303 (M^+, 6), 261 (M^+ − C_3H_7, 9), 223 (24), 181 (57), 139 (92) and 124 (100) (Found: C, 59.7; H, 5.8; N, 13.5. $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.65; N, 13.85%).

4-(3-Isopropoxy-6-methoxyanilino)-3-nitropyridine **31b**. The product was crystallised from aqueous methanol to give the *title compound* **31b** (70%), m.p. 81–83 °C; ν_{max}/cm^{-1} (KBr) 3320 (NH) and 1560 and 1360 (NO_2); $\delta_H[(CD_3)_2CO]$ 1.28 (6 H, d, *J* 7, 2 × CH_3), 3.83 (3 H, s, OCH_3), 4.55 (1 H, heptet, *J* 6, CH), 6.89 (1 H, dd, *J* 10 and 3, 4′-H), 7.04 (3 H, m, 5-H and 2′- and 5′-H), 8.30 (1 H, d, *J* 7, 6-H), 9.16 (1 H, s, 2-H) and 9.59 (1 H, s, exchanged with D_2O, NH); *m/z* (%) 303 (M^+, 51), 261 (100), 246 (88), 200 (49) and 149 (41) (Found: C, 59.6; H, 5.7; N, 13.5, $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.65; N, 13.85%).

Reduction of the 3-*Nitropyridines* **11**, **19**, **31a** *and* **31b** *to Give the* 3-*Aminopyridines* **12**, **20**, **32a** *and* **32b**, *respectively: General Method*.—A methanolic solution of **11**, **19**, **31a** and **31b** was reduced with hydrogen at atmospheric pressure and room temperature in the presence of palladium on charcoal (10%) until the uptake of hydrogen ceased (2–5 h). The solid was removed and the solution evaporated to yield a viscous liquid.

3-Amino-2-(3-methoxyanilino)pyridine **12**. This compound, obtained by chromatography of the oil (ethyl acetate–light petroleum, 1:1) was a solid (86%) which was recrystallised from diisopropyl ether, m.p. 105–106 °C; ν_{max}/cm^{-1} (KBr) 3440 (NH) and 3240 and 3160 (NH_2); $\delta_H(CDCl_3)$ 3.28 (2 H, br s, exchanged with D_2O, NH_2), 3.75 (3 H, s, 3′-OCH_3), 6.19 (1 H, br s, exchanged with D_2O, NH) 6.40 (1 H, dd, *J* 6 and 2, 6′-H), 6.48 (1 H, dd, *J* 5 and 2, 4′-H), 6.66 (1 H, m, 5′-H), 6.75 (1 H, m, 2′-H), 6.89 (1 H, m, 5-H), 7.10 (1 H, dd, *J* 5 and 2, 4-H) and 7.78 (1 H, dd, *J* 5 and 2, 6-H); *m/z* (%) 215 (M^+, 83), 214 (100), 200 (M^+ − CH_3, 30), 199 (40) and 149 (92) (Found: C, 66.7; H, 6.1; N, 19.4. $C_{12}H_{13}N_3O$ requires C, 67.0; H, 6.1; N, 19.5%).

3-Amino-2-(2-isopropoxy-5-methoxyanilino)pyridine **20**. This compound, purified by chromatography (ethyl acetate–light

petroleum, 1:9) and crystallisation of the resultant solid from light petroleum, formed colourless needles (74%), m.p. 84–85 °C; ν_{max}/cm^{-1} (KBr) 3390 and 3320 (NH_2); $\delta_H(CDCl_3)$ 1.35 (6 H, d, *J* 6, 2 × CH_3), 3.40 (3 H, br s, exchanged with D_2O, NH_2), 3.78 (3 H, s, OCH_3), 4.44 (1 H, heptet, *J* 6, CH), 6.38 (1 H, dd, *J* 8 and 2, 4'-H), 6.72 (1 H, m, 5-H), 6.82 (1 H, d, *J* 8, 3'-H), 6.99 (1 H, dd, *J* 8 and 2, 4-H), 7.77 (1 H, d, *J* 2, 6'-H), 7.85 (1 H, dd, *J* 2 and 5, 6-H) and 10.15 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 273 (M^+, 26), 230 ($M^+ - C_3H_7$, 51) 214 ($M^+ - OC_3H_7$, 100) and 199 (35) (Found: C, 65.7; H, 7.0; N, 15.4. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%).

3-*Amino*-4-(2-*isopropoxy*-5-*methoxyanilino*)*pyridine* **32a**. This compound, purified by flash column chromatography (ethyl acetate–light petroleum, 1:7) and by use of a Chromatotron (silica gel, ethyl acetate–light petroleum), was obtained as a colourless oil (59%), b.p. 158–160 °C at 0.3 mmHg; ν_{max}/cm^{-1} (liq.) 3380–3200 (NH_2 and NH); $\delta_H(CDCl_3)$ 1.32 (6 H, d, *J* 6, 2 × CH_3), 3.72 (2 H, br s, exchanged with D_2O, NH_2), 3.75 (3 H, s, OCH_3), 4.40 (1 H, heptet, *J* 6, CH), 6.24 (1 H, br s, exchanged with D_2O, NH), 6.42–6.89 (3 H, m, 3'-, 4'- and 6'-H), 7.15 (1 H, d, *J* 6, 5-H), 7.97 (1 H, d, *J* 6, 6-H) and 8.07 (1 H, s, 2-H); *m/z* (%) 273 (M^+, 100), 256 (65), 231 (88), 200 (32), 199 (71) and 170 (35) (Found: C, 65.9; H, 7.2; N, 15.3. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%).

3-*Amino*-4-(3-*isopropoxy*-6-*methoxyanilino*)*pyridine* **32b**. This compound was obtained (93%) by distillation of the oil, b.p. 128–130 °C at 0.2 mmHg; ν_{max}/cm^{-1} (liq.) 3400 (NH_2 and NH); $\delta_H[(CD_3)_2CO]$ 1.25 (6 H, d, *J* 7, 2 × CH_3), 2.89 (3 H, s, exchanged with D_2O, NH and NH_2), 3.78 (3 H, s, OCH_3), 4.44 (1 H, heptet, *J* 6, CH), 6.45 (1 H, dd, *J* 9 and 3, 4'-H), 6.84 (3 H, m, 5-H and 2'- and 5'-H), 7.77 (1 H, d, *J* 6, 6-H) and 8.0 (1 H, s, 2 H); *m/z* (%) 273 (M^+, 60), 256 (49), 231 (46) and 149 (100) (Found: M^+, 273.1477. $C_{15}H_{19}N_3O_2$ requires M^+, 273.1477).

Preparation of the 1,2,3-*Triazolopyridines* **13**, **21**, **33a** and **33b**: *General Method*.—Cold aqueous sodium nitrite (1.5 mol equiv.) was added dropwise to a stirred solution of the appropriate 3-aminopyridine in an excess of dilute hydrochloric acid (0.1 mol dm^{-3}) maintained at 0 °C. Stirring was continued at 0 °C for a further 10 min after which the mixture was allowed to reach room temperature; it was then stirred at this temperature for 30 min. The product was either filtered off or extracted from the reaction mixture with diethyl ether.

3-(3-*Methoxyphenyl*)-3H-1,2,3-*triazolo*[4,5-b]*pyridine* **13**. This compound, obtained as a solid and crystallised from light petroleum, formed colourless needles (95%), m.p. 83–84 °C (lit.,[14] m.p. 78–80 °C); $\delta_H(CDCl_3)$ 3.90 (3 H, s, OCH_3), 6.94 (1 H, dd, *J* 2 and 5, 6'-H), 7.33 (2 H, m, 2'- and 4'-H), 7.86 (2 H, m, 6- and 5'-H), 8.40 (1 H, dd, *J* 8 and 2, 7-H), 8.71 (1 H, dd, *J* 5 and 2, 5-H); *m/z* (%) 226 (M^+, 16), 199 (14), 198 ($M^+ - N_2$, 100) and 155 (43).

3-(2-*Isopropoxy*-5-*methoxyphenyl*)-3H-1,2,3-*triazolo*[4,5-b]-*pyridine* **21**. This compound, obtained as an oil from the ethereal extract, was distilled to give a pale yellow viscous oil (90%), b.p. 150–155 °C at 0.4 mmHg; $\delta_H(CDCl_3)$ 1.03 (6 H, d, *J* 6, 2 × CH_3), 3.83 (3 H, s, OCH_3), 4.03 (1 H, heptet, *J* 6, CH), 7.10 (3 H, m, 3'-, 4'- and 6'-H), 7.39 (1 H, m, 6-H), 8.46 (1 H, dd, *J* 8 and 2, 7-H) and 8.71 (1 H, dd, *J* 5 and 2, 5-H); *m/z* (%) 284 (M^+, 14), 241 ($M^+ - C_3H_7$, 25) 214 (100), 199 (95) and 178 (58) (Found: C, 63.4; H, 5.7; N, 19.4. $C_{15}H_{16}N_4O_2$ requires C, 63.4; H, 5.7; N, 19.7%).

1-(2-*Isopropoxy*-5-*methoxyphenyl*)-1H-1,2,3-*triazolo*[4,5-c]-*pyridine* **33a**. This compound, obtained by evaporation of the extract, flash chromatography of the residue (ethyl acetate–light petroleum, 1:4) and distillation of the major fraction, was a pale yellow oil (71%), b.p. 136–140 °C at 1 mmHg; $\delta_H(CDCl_3)$ 1.04 (6 H, d, *J* 6, 2 × CH_3), 3.84 (3 H, s, OCH_3), 4.31 (1 H, heptet, *J* 6, CH), 7.10 (3 H, m, 7-, 3'- and 6'-H), 7.44 (1 H, d, *J* 6, 4'-H), 8.57 (1 H, d, *J* 6, 6-H) and 9.53 (1 H, s, 4-H); *m/z* (%) 284 (M^+, 12), 213 (42), 199 (100) and 171 (50) (Found: C, 63.3; H, 5.7; N, 19.4. $C_{15}H_{16}N_4O_2$ requires C, 63.4; H, 5.7; N, 19.7%).

1-(3-*Isopropoxy*-6-*methoxyphenyl*)-1H-1,2,3-*triazolo*[4,5-c]-*pyridine* **33b**. This compound, initially an oil, was chromatographed (ethyl acetate–light petroleum, 1:1) to give a solid which after recrystallisation from diisopropyl ether, afforded a colourless solid (75%), m.p. 76–78 °C; $\delta_H(CDCl_3)$, 1.34 (6 H, d, *J* 6, 2 × CH_3), 3.76 (3 H, s, OCH_3), 4.51 (1 H, heptet, *J* 6, CH), 7.13 (3 H, m, 7-, 3'- and 6'-H), 7.36 (1 H, dd, *J* 5 and 1, 4'-H), 8.57 (1 H, d, *J* 5, 6-H) and 9.53 (1 H, s, 4-H); *m/z* (%) 284 (M^+, 6), 241 (14), 199 (100) and 149 (38) (Found: C, 63.35; H, 5.8; N, 19.65. $C_{15}H_{16}N_4O_2$ requires C, 63.4; H, 5.7; N, 19.7%).

Procedure for the Photo-Graebe–Ullmann Reaction to give the Dialkoxycarbolines **22**, **34a** and **34b**, *the Methoxycarbolines* **9a** *and* **14** *and Isopropoxycarboline* **35**.—A dilute solution (*ca.* 5 mmol) of the alkoxy- or dialkoxy-triazolopyridine in methanol was stirred and irradiated under nitrogen. The methanol was evaporated to give an oil.

9-*Methoxy*-5H-*pyrido*[2,3-b]*indole* (9-*methoxy*-α-*carboline*) **14** *and* 7-*methoxy*-5H-*pyrido*[2,3-b]*indole* (7-*methoxy*-α-*carboline*) **9a**. These compounds were obtained after irradiation of the triazolopyridine **13** for 24 h. Careful flash chromatography (ethyl acetate–light petroleum, 1:4) gave a solid which crystallised from diisopropyl ether to afford the α-*carboline* **14** (49%), m.p. 215–216 °C; ν_{max}/cm^{-1} (KBr) 3420 (NH); $\delta_H(CDCl_3)$ 4.08 (3 H, s, OCH_3), 6.72 (1 H, d, *J* 8, 8-H), 7.19 (2 H, m, 6- and 7-H), 7.42 (1 H, t, 3-H), 8.46 (1 H, dd, *J* 2 and 5, 2-H), 8.53 (1 H, dd, *J* 8 and 2, 1-H) and 10.74 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 199 ($M^+ + H$, 14), 198 (M^+, 100), 183 ($M^+ - CH_3$) and 155 (58) (Found: C 72.65; H, 5.3; N 14.0. $C_{12}H_{10}N_2O$ requires C, 72.75; H, 5.1; N, 14.1%).

The second major component from the chromatography column was shown to be 7-methoxy-α-carboline **9a** (43%), by comparison of its m.p. and IR and NMR spectra with those of an authentic sample.[5]

6-*Isopropoxy*-9-*methoxy*-5H-*pyrido*[2,3-b]*indole* (6-*isopropoxy*-9-*methoxy*-α-*carboline*) **22** *and* 7-*methoxy*-α-*carboline* **9a**. These compounds were obtained by photolysis of the triazolopyridine **21** for 48 h and flash chromatography (ethyl acetate–light petroleum, 1:8). The major component was crystallised from diethyl ether to give the α-*carboline* **22** (84%), m.p. 175–176 °C; ν_{max}/cm^{-1} (KBr) 3440 (NH); $\delta_H(CDCl_3)$ 1.43 (6 H, d, *J* 6, 2 × CH_3), 4.03 (3 H, s, OCH_3), 4.64 (1 H, heptet, *J* 6, CH), 6.57 (1 H, d, *J* 9, 8-H), 6.93 (1 H, d, *J* 9, 7-H), 7.18 (1 H, m, 2-H), 8.52 (2 H, m, 1- and 3-H) and 10.45 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 257 (M + H, 12), 256 (M^+, 63), 214 ($M^+ - C_3H_7$, 100) and 199 (79) (Found: C, 70.2; H, 6.2; N, 10.85. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%). 7-Methoxy-α-carboline **9a** (9%) was obtained as the second major fraction from the chromatography column.

6-*Isopropoxy*-9-*methoxy*-5H-*pyrido*[3,4-b]*indole* (6-*isopropoxy*-9-*methoxy*-γ-*carboline*) **34a**. This compound, produced when the triazolopyridine **33a** was irradiated for 48 h and the product purified by flash chromatography (ethyl acetate–light petroleum, 1:7) and crystallisation from light petroleum–chloroform, formed cream microcrystals (36%), m.p. 233–234 °C (decomp. from 200 °C); ν_{max}/cm^{-1} (KBr) 3460 (NH); $\delta_H(CDCl_3)$ 1.40 (6 H, d, *J* 6, 2 × CH_3), 4.04 (3 H, OCH_3), 4.64 (1 H, heptet, *J* 6, CH), 6.59 (1 H, d, *J* 9, 7-H), 6.89 (1 H, d, *J* 9, 8-H), 7.33 (1 H, d, *J* 6, 4-H), 8.51 (1 H, d, *J* 6, 3-H) 9.45 (1 H, s, 1-H) and 9.81 (1 H, s, exchanged with D_2O, NH); *m/z* 256 (M^+, 46), 214 ($M^+ - C_3H_7$, 98), 199 (100) and 171 (16); TLC gave R_f 0.51 with methanol–chloroform (1:4) (Found: M^+, 256.1212. $C_{15}H_{16}N_2O_2$ requires M^+, 256.1211).

9-*Isopropoxy*-6-*methoxy*-5H-*pyrido*[3,4-b]*indole* (9-*isopropoxy*-6-*methoxy*-γ-*carboline*) **34b**. This compound was obtained

from the triazolopyridine **33b** by irradiation for 8 h and purification of the crude product by flash column chromatography (ethyl acetate–light petroleum, 2:3) and then preparative TLC (ethyl acetate–light petroleum, 2:3). The product was crystallised from aqueous methanol to give the *title compound* **34b** (30%), m.p. 284–285 °C; ν_{max}/cm^{-1} (KBr) 3460 (NH); $\delta_H[(CD_3)_2SO]$ 1.41 (6 H, d, *J* 6, 2 × CH_3), 3.92 (3 H, s, OCH_3), 4.75 (1 H, heptet, *J* 6, CH), 6.66 (1 H, d, *J* 8, 7-H), 6.94 (1 H, d, *J* 8, 8-H), 7.36 (1 H, d, *J* 7, 4-H), 8.34 (1 H, d, *J* 7, 3-H), 9.22 (1 H, s, 1-H) and 11.4 (1 H, br s, exchanged with D_2O, NH): *m/z* (%) 256 (M^+, 39), 214 (68), 199 (100) and 149 (26) (Found: C, 69.2; H, 6.2; N, 10.7. $C_{15}H_{16}N_2O_2 \cdot 0.25H_2O$ requires C, 69.1; H, 6.3; N, 10.7%).

7-*Isopropoxy*-5H-*pyrido*[3,4-b]*indole* (7-*isopropoxy*-γ-*carboline*) **35**. This compound, obtained as the second fraction from column chromatography and purified by preparative TLC (methanol–chloroform, 1:19), gave the cream coloured *ether* **35** (15%), m.p. 240–242 °C; ν_{max}/cm^{-1} 3460 (NH); $\delta_H[(CD_3)_2SO]$ 1.31 (6 H, d, *J* 6, 2 × CH_3), 4.68 (1 H, heptet, *J* 6, CH), 6.84 (1 H, dd, *J* 9 and 3, 8-H), 7.01 (1 H, d, *J* 3, 6-H), 7.37 (1 H, d, *J* 5, 4-H), 8.03 (1 H, d, *J* 9, 9-H), 8.31 (1 H, d, *J* 5, 3-H), 9.17 (1 H, s, 1-H) and 11.40 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 226 (M^+, 36), 184 (100) and 155 (25) (Found: C, 74.0; H, 6.2; N, 12.2. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.2; N, 12.4%).

3-(N-*Acetyl*-2,5-*dimethoxyanilino*)*pyridine* **39**.—A mixture of 2,5-dimethoxyacetanilide[15] (1.5 g), 3-bromopyridine (15 cm^3), anhydrous potassium carbonate (1.5 g) and activated copper bronze[16] (6 g) was stirred and refluxed under a nitrogen atmosphere for 6 h. The solid was filtered off and washed with chloroform. The combined washings and filtrate were evaporated, and the residue was taken up in chloroform and the solution washed with water. Evaporation of the extract yielded a brown oil which, purified by flash chromatography (ethyl acetate–light petroleum, 1:4), gave a solid. Crystallisation of this from diethyl ether gave the *title compound* **39** (1.1 g, 53%), m.p. 89–90 °C; ν_{max}/cm^{-1} (KBr) 1670 (CO); $\delta_H(CDCl_3)$ 2.0 (3 H, s, CH_3), 3.72 (3 H, s, 2-OCH_3), 3.77 (3 H, s, 5-OCH_3), 6.81 (3 H, m, 3'-, 4'- and 6'-H), 7.17 (1 H, m, 5-H), 7.65 (1 H, m, 4-H), 8.33 (1 H, dd, *J* 5 and 1, 6-H) and 8.46 (1 H, d, *J* 1, 2-H); *m/z* (%) 272 (M^+, 39), 230 ($M^+ - CH_2CO$, 51) and 215 (100) (Found: C, 66.2; H, 5.9; N, 10.2. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%).

3-(2,5-*Dimethoxyanilino*)*pyridine* **40**.—Sodium hydroxide (3.65 g) in methanol (70 cm^3) was added to the pyridine **39** (1 g) in methanol (40 cm^3) and the mixture refluxed for 40 min under a nitrogen atmosphere. It was then poured into water and extracted with diethyl ether. The extract was evaporated to give a solid which was crystallised from diethyl ether to afford the *title compound* **40** (0.72 g, 86%), m.p. 92–93 °C; ν_{max}/cm^{-1} (KBr) 3240 (NH); $\delta_H(CDCl_3)$ 3.71 (3 H, s, 2-OCH_3), 3.83 (3 H, s, 5-OCH_3), 6.12 (1 H, br s, exchanged with D_2O, NH), 6.35 (1 H, dd, *J* 9 and 3, 4'-H), 6.77 (2 H, m, 3'- and 6'-H), 7.10 (1 H, m, 5-H), 7.47 (1 H, m, 4-H), 8.14 (1 H, d, *J* 2, 6-H) and 8.38 (1 H, s, 2-H); *m/z* (%) 230 (M^+, 76), 215 ($M^+ - CH_3$, 100) and 200 (27) (Found: C, 67.9; H, 6.1; N, 12.3. $C_{13}H_{14}N_2O_2$ requires C, 67.8; H, 6.1; N, 12.2%).

6,9-*Dimethoxy*-5H-*pyridine*[3,2-b]*indole* (6,9-*Dimethoxy*-δ-*carboline*) **41**.—The pyridine **40** (0.7 g) in dry THF (600 cm^3) was stirred and photolysed for 38 h under a nitrogen atmosphere. The solvent was evaporated and the residue separated by flash chromatography (ethyl acetate–light petroleum, 3:2) into starting material (0.27 g) and a product which was crystallised from chloroform–light petroleum. This afforded the δ-*carboline* **41** (0.16 g, 37% based on recovered starting material), m.p. 220–221 °C; ν_{max}/cm^{-1} (KBr) 3100 (NH); $\delta_H(CDCl_3)$ 4.01 (3 H, s, 9-OCH_3), 4.06 (3 H, s, 6-OCH_3), 6.55 (1 H, d, *J* 9, 8-H), 6.85 (1 H, d, *J* 9, 7-H), 7.25 (1 H, m, 3-H), 7.67 (1 H, dd, *J* 8 and 2, 4-H), 8.31 (1 H, br s, exchanged with D_2O, NH) and 8.6 (1 H, dd, *J* 5 and 2, 2-H); *m/z* (%) 228 (M^+, 92) 213 ($M^+ - CH_3$, 100), 200 (74) and 184 (46) (Found: C, 68.3; H, 5.2; N, 12.2. $C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.3; N, 12.3%).

Preparation of the Carbolinequinones **37**, **38** *and* **42** *by Oxidation of Dialkoxycarbolines with Ceric Ammonium Nitrate (CAN): General method.*—A solution of CAN (0.9 g) in water (10 cm^3) was added dropwise to a stirred solution of the dialkoxycarboline (0.1 g) in glacial acetic acid (10 cm^3). The mixture became dark red and then orange or yellow. Stirring was continued for 3.5 h after which the solid was filtered off and the quinone isolated from the filtrate.

9*H*-*Pyrido*[2,3b]*indole*-5,8-*dione* (α-*carboline*-6,9-*quinone*) **37**. Compound **37**, obtained when the solution was evaporated to a small volume and poured into ice–water, was filtered off and crystallised from chloroform. It was identical with an authentic sample.[5]

5H-*Pyrido*[3,4-b]*indole*-6,9-*dione* (γ-*carboline*-6,9-*quinone*) **38**. Compound **38** was extracted into chloroform from the neutralised filtrate. The extract was evaporated to leave a dark red solid which crystallised from methanol–light petroleum to give the *title compound* (50%) homogeneous by TLC (R_f 0.43; methanol–chloroform, 1:9), m.p. > 300 °C (decomp. from 200 °C); ν_{max}/cm^{-1} (KBr) 3190 (NH), 1680 (CO) and 1640 (CO); $\delta_H(CDCl_3)$ 6.88 (2 H, s, 7- and 8-H), 7.36 (1 H, d, *J* 6, 4-H), 8.54 (1 H, d, *J* 6, 3-H), 9.63 (1 H, s, 1-H) and 12.35 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 198 (M^+, 100), 170 ($M^+ - CO$, 39), 143 (44) and 116 (30) (Found: M^+, 198.0429. $C_{11}H_6N_2O_2$ requires M^+, 198.0429).

5H-*Pyrido*[3,2-b]*indole*-6,9-*dione* (δ-*carboline*-6,9-*quinone*) **42**. The compound was obtained by basification (pH 9) of the filtrate with saturated aqueous sodium hydrogen carbonate and extraction with chloroform. Evaporation of the extract gave a residue which was crystallised from chloroform to give the orange δ-*carboline quinone* (58%) homogeneous by TLC (R_f 0.22; methanol–chloroform, 1:19), m.p. > 300 °C (decomp. from 210 °C); ν_{max}/cm^{-1} (KBr) 3450 (NH), 1680 (CO) and 1660 (CO); $\delta_H[(CD_3)_2SO]$ 6.76 (2 H, s, 7- and 8-H), 7.34 (1 H, m, 3-H), 7.92 (1 H, dd, *J* 8 and 2, 4-H), 8.59 (1 H, dd, *J* 5 and 2, 2-H) and 12.97 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 198 (M^+, 100), 170 ($M^+ - CO$, 26), 149 (60) and 144 (39) (Found: M^+, 198.0429. $C_{11}H_6N_2O_2$ requires M^+, 198.0429).

9-*Hydroxy*-5H-*pyrido*[2,3-b]*indole* (9-*hydroxy*-α-*carboline*) **36**.—The pyridoindole **9a** (0.38 g) in hydrobromic acid (47%; 25 cm^3) was refluxed for 4 h after which the mixture was evaporated to dryness under reduced pressure. The hydrobromide salt was dissolved in water and the solution basified to pH 9 by the addition of aqueous sodium hydrogen carbonate. The precipitate crystallised from diisopropyl ether to give the *title compound* (0.33 g, 94%), m.p. 170–171 °C; ν_{max}/cm^{-1} (KBr) 3440 (OH) and 3180 (NH); $\delta_H[(CD_3)_2SO]$ 5.32 (1 H, br s, exchanged with D_2O, 9-OH), 6.83 (1 H, d, *J* 8, 8-H), 7.13 (1 H, d, *J* 8, 6-H), 7.44 (2 H, t, 3- and 7-H), 8.52 (1 H, dd, *J* 5 and 2, 2-H), 8.82 (1 H, dd, *J* 8 and 2, 1-H) and 12.58 (1 H, br s, exchanged with D_2O, NH); *m/z* (%) 184 (M^+, 100), 156 (12) and 155 (30) (Found: C, 72.1; H, 4.3; N, 15.2. $C_{11}H_8N_2O$ requires C, 72.5; H, 4.4; N, 15.4%).

9H-*Pyrido*[2,3-b]*indole*-5,8-*dione* (α-*carboline*-6,9-*quinone*) **37**. This compound was also obtained when 9-hydroxy-α-carboline (50 mg) in methanol (25 cm^3) was added dropwise to a stirred mixture of potassium dihydrogen phosphate (120 mg) and Fremy's salt (1.25 g) in water (55 cm^3). Stirring was continued for 2 h after which the mixture was extracted with

chloroform. The extract yielded a red solid which was purified by flash chromatography (methanol–chloroform, 1:99) to give the α-carboline quinone, identical with that obtained previously.

Acknowledgements

We thank the SERC Mass Spectrometry Service, Swansea, for the high resolution mass spectral data.

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Paper 2/05896K
Received 4*th November* 1992
Accepted 4*th March* 1993