[2,3] Fused Indoles. Part 2.[1] Synthesis of 1,8-Dihydropyrrolo[2,3-*b*]indoles, and Photochemical Rearrangement of their 1-Allyl Derivatives[2]

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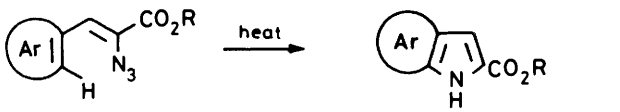
1,8-Dihydropyrrolo[2,3-*b*]indoles (**6**) are prepared in three steps from indole-3-carbaldehyde *via* the azidoacrylates (**2**). The 2-ester substituent is readily hydrolysed and decarboxylated, whereas attempted reduction leads to bis(pyrroloindolyl)methanes (**16**). The 1-allyl (**21**), methylallyl and prenyl derivatives (**24a**) and (**24b**) undergo photochemical rearrangement to the 2*H*-isomers (**23**), (**25a**), and (**25b**) respectively in a reaction typical of pyrroles.

The thermal decomposition of α-azido acrylates bearing a β-aryl or hetaryl substituent constitutes a useful route to indoles and other fused pyrroles (Scheme 1).[3] In continuation of our



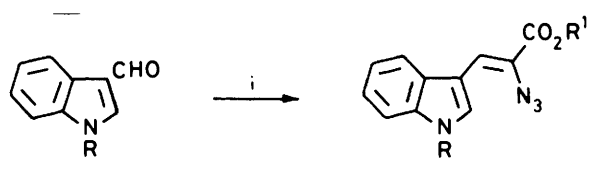
Ar = aryl, hetaryl

Scheme 1.

work on the synthesis of [2,3] fused indoles,[1] we have investigated the thermal decompositon of α-azido-β-indol-3-ylacrylates as a route to the pyrrolo[2,3-*b*]indole ring system. We now report our results in full.

Results and Discussion

The starting azides (**2**) (31—81%) were prepared by condensation of the corresponding 1-alkylindole-3-carbaldehydes (**1**) (Scheme 2) with ethyl or methyl azidoacetate under the usual



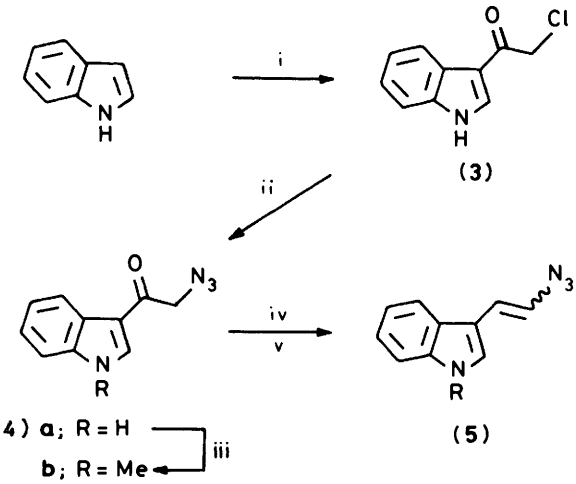
(**1**) (**2**)

a; R = Me
b; R = CH_2Ph
c; R = CH_2OMe

a; R = Me, R^1 = Et
b; R = CH_2Ph, R^1 = Et
c; R = CH_2OMe, R^1 = Et
d; R = CH_2OMe, R^1 = Me

Scheme 2. *Reagents:* i, $R^1O_2CCH_2N_3$, $NaOR^1$, R^1OH, −10 °C

conditions.[1] Indole-3-carbaldehyde itself did not react. The azides (**2**) are crystalline solids which can be stored without extensive decomposition in a refrigerator. For comparison, the vinyl azides (**5**) which lack the ester substituent were also prepared, by a route analogous to that used for the preparation of β-azidostyrene from phenacyl bromide.[4] Thus, reaction of indole with chloroacetyl chloride in toluene containing pyridine gave 3-chloroacetylindole (**3**).[5] Treatment of (**3**) with sodium azide afforded the corresponding azidoketone (**4a**) quantitatively. Reduction of (**4a**) with sodium borohydride followed by dehydration (methanesulphonyl chloride–triethylamine) gave the vinyl azide (**5a**) as a mixture of *cis*/*trans* isomers. The *N*-methyl vinyl azide (**5b**) was prepared by *N*-methylation at the azidoketone stage to give (**4b**) followed by reduction and dehydration (Scheme 3). The vinyl azides (**5**) are consider-

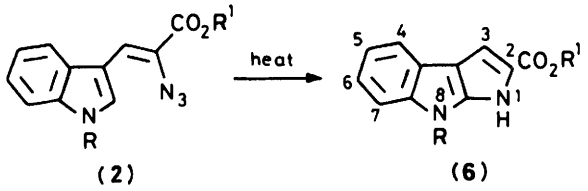


Scheme 3. *Reagents:* i, $ClCH_2COCl$, pyridine, toluene, 60 °C; ii, NaN_3, aqueous acetone; iii, MeI, K_2CO_3, acetone; iv, $NaBH_4$, EtOH, AcOH; v, $MeSO_2Cl$, CH_2Cl_2, Et_3N

ably less stable than the azido acrylates (**2**), and darken rapidly on exposure to light at room temperature.

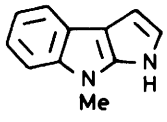
Thermolysis of the azido acrylates (**2**) in boiling toluene (1—2 h) resulted in loss of nitrogen and cyclisation to the 1,8-dihydropyrrolo[2,3-*b*]indole-2-carboxylates (**6**) in good yield (70—94%). In contrast, heating of the azides (**5**) in toluene (5 min) resulted in rapid darkening of the solution. Although decomposition of the *N*-substituted azide (**5a**) gave a complex mixture, the *N*-methyl compound (**5b**) gave largely one product as an unstable oil, the n.m.r. spectrum of which is consistent with the pyrroloindole (**7**).

Although the pyrrolo[2,3-*b*]indole system occurs in nature at the hexahydro level in alkaloids such as physostigmine (**8**),[6] aszonalenin (**9**),[7] and the structurally related neurotoxin roquefortine (**10**),[8] little is known about the less saturated versions of this ring system.[9] With a view to developing routes to these latter two alkaloids, the 1,8-dihydropyrrolo[2,3-*b*]indoles (**6**) seemed useful intermediates since they are easily



(2) (6)

a; R = Me, R^1 = Et
b; R = CH_2Ph, R^1 = Et
c; R = CH_2OMe, R^1 = Et
d; R = CH_2OMe, R^1 = Me



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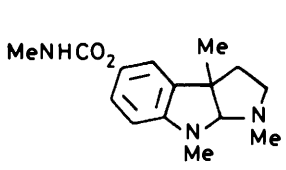

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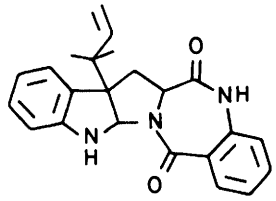

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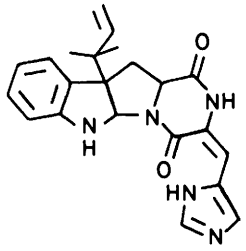
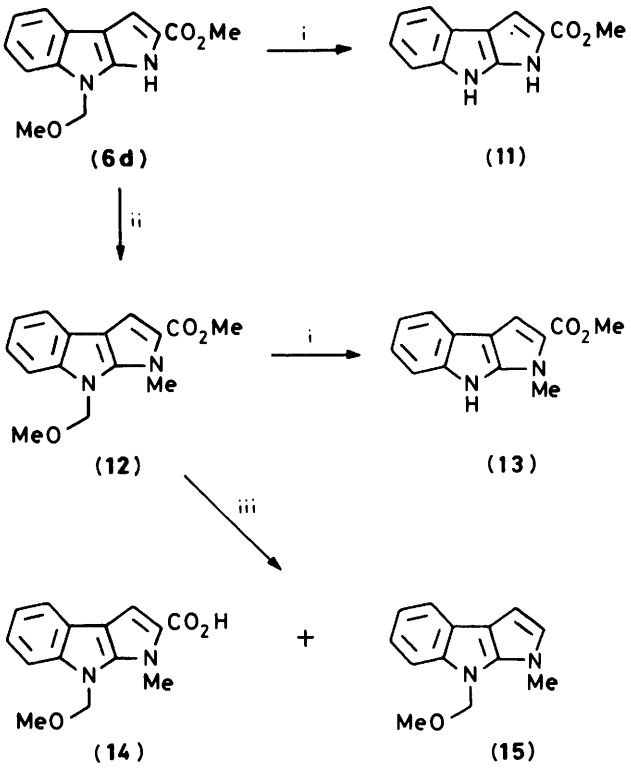


(10)

prepared in three steps from indole-3-carbaldehyde, and they offer some scope for the introduction of the substituent at C-3a and for the annelation of the fourth ring between N-1 and the carbonyl at C-2.

Standard transformations of methyl 1,8-dihydro-8-methoxymethylpyrrolo[2,3-*b*]indole-2-carboxylate (**6d**) proceeded without incident. Thus the methoxymethyl group was cleaved by treatment, for an extended period (2 weeks), with dilute hydrochloric acid in methanol at room temperature to give the pyrroloindole (**11**). Attempts to accelerate the rate of deprotection by the use of higher temperatures or stronger acid resulted only in decomposition. The pyrroloindole (**6d**) readily forms a sodium salt on treatment with sodium hydride in dimethylformamide (DMF) at room temperature. Subsequent reaction of the salt with iodomethane gave the 1-methyl derivative (**12**). Treatment of (**12**) with dilute hydrochloric acid in methanol results in deprotection and formation of the 8-unsubstituted derivative (**13**). Curiously, the methoxymethyl group is cleaved from (**12**) much faster than from (**6d**).

Hydrolysis of the *N*-methyl compound (**12**) in alkaline

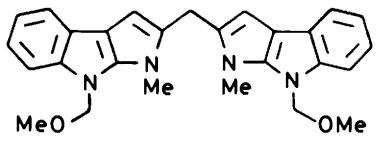


(6d) (11) (12) (13) (14) (15)

Scheme 4. *Reagents:* i, dilute HCl, MeOH, room temp; ii, NaH, DMF, MeI; iii, NaOH, MeOH–H_2O, reflux, then acid work-up

solution gave the corresponding carboxylic acid (**14**) (45%) together with the decarboxylated product (**15**) (24%). This comparative ease of decarboxylation is in contrast to pyrrole- and indole-carboxylic acids which often require more vigorous conditions. The decarboxylated product (**15**) is an unstable oil, which shows similar properties to compound (**7**).

Reduction of (**12**) with lithium aluminium hydride (LAH) (2 equiv.) in tetrahydrofuran (THF) gave, unexpectedly, the bis(pyrroloindolyl)methane (**16**). The reduction of simple 2-carbonylpyrroles with LAH has been well studied, and it is known that reduction of pyrrole-2-carboxylic esters gives 2-methylpyrroles when large excesses of LAH are used. With equimolar amounts of LAH, dipyrromethanes can be isolated.[10] However, reduction of 1-methylpyrrole-2-carboxylic esters, even with a large excess of LAH gives only 2-hydroxymethyl-1-methylpyrrole.[11] The LAH reduction of (**12**) therefore provides something of a contrast, since only the bis(pyrroloindolyl)methane (**16**) was formed, with no evidence

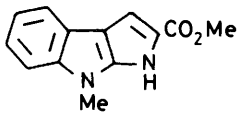


(16)

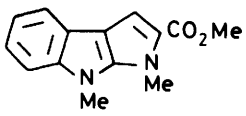
for any 2-methyl or 2-hydroxymethyl derivatives being obtained.

The reaction of the 1,8-dihydropyrrolo[2,3-*b*]indoles with other reducing agents was investigated briefly. Thus treatment of (**6d**) with borane–trimethylamine complex in dioxane containing dilute hydrochloric acid gave the corresponding 8-methyl compound (**17**) (32%). A similar reduction of the *N*-

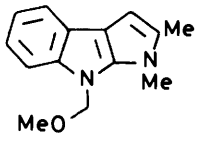
methoxymethyl group to *N*-methyl was observed when (**12**) was treated with an excess of sodium cyanoborohydride in acetic acid to give the 1,8-dimethyl compound (**18**) in high yield. Reaction of (**12**) with 'copper(I) hydride' [from copper(I) bromide and sodium bis(2-methoxyethoxy)aluminium hydride [12]] however, resulted in reduction of the ester substituent to a methyl group and the formation of (**19**) (17%), together with



(**17**)



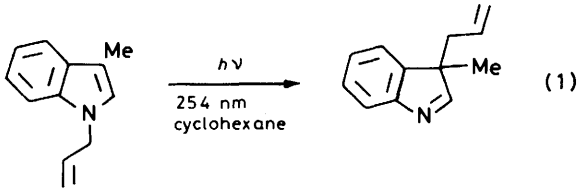
(**18**)



(**19**)

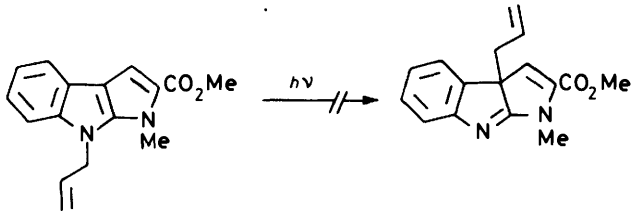
the bis(pyrroloindolyl)methane (**16**) (16%) and returned starting material. There was no evidence for any reduction of the 2,3-double bond in any of the above reactions.

Attention was then turned to the introduction of an allyl substituent at C-3a, and, based on the report [13] that irradiation of 1-allyl-3-methylindole gives 3-allyl-3-methylindolenine [equation (1)], the transfer of allyl groups from nitrogen to



(1)

carbon was investigated. Accordingly, methyl 8-allyl-1,8-dihydro-1-methylpyrrolo[2,3-*b*]indole-2-carboxylate (**20**) was prepared by treatment of (**13**) with sodium hydride in dimethylformamide (DMF) followed by allyl bromide. However, compound (**20**) was unchanged after irradiation in cyclohexane at 300 nm and at 254 nm. Compound (**20**) when heated in benzene in the presence of aluminium chloride, conditions which are also reported to effect rearrangement of *N*-allylindoles,[14] decomposed completely.

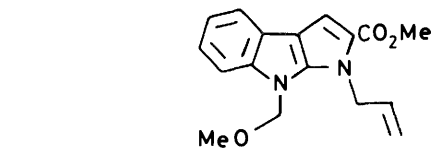


(**20**)

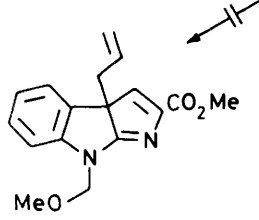
The failure to transfer an allyl group from N-8 to carbon prompted an investigation into the corresponding N-1 substituted derivatives. Reaction of the pyrroloindole (**6d**) with sodium hydride in DMF followed by allyl bromide gave the required 1-allyl derivative (**21**) (71%) together with a minor product (13%).

Although the *N*-allyl compound (**21**) was recovered after being heated in decalin for 24 h, it was rapidly converted into another compound by irradiation in cyclohexane at 300 nm for 40 min. A small amount (11%) of the pyrroloindole (**6d**) was also formed by photochemical cleavage of the allyl group. The major product (62%), an isomer of starting material, was shown to be identical with the minor product formed in the allylation reaction. That the allyl group had migrated from nitrogen to carbon was immediately clear from the n.m.r. spectra, although the data was equally consistent with the required 3a-allyl isomer (**22**) and the 2-allyl isomer (**23**). However, the presence of an ester carbonyl at 1 730 cm^{-1} suggested that the product was, in fact, the 2-isomer (**23**), and this assignment was confirmed by an *X*-ray crystallographic study.*

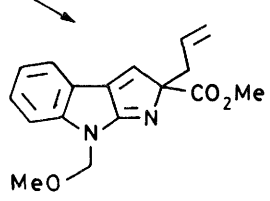
The fact that the N-1 allyl derivative rearranges exclusively to the 2*H*-isomer (**23**) suggests that the terminal five-membered ring of the 1,8-dihydropyrroloindole system behaves as an isolated pyrrole, since *N*-allylpyrroles are known to undergo photochemical rearrangement to 2*H*-pyrroles.[15] On the other hand, if the system showed any indole-like character the formation of the 3a-isomer (**22**) was expected, since another indole which bears a 2-allyl hetero atom substituent is reported [16] to undergo facile rearrangement with transfer of the allyl group to the 3-position [equation (2)].



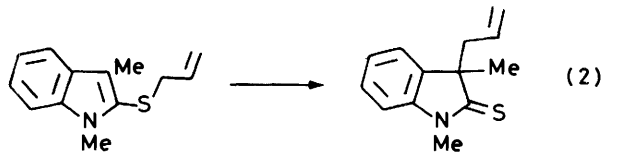
(**21**)



(**22**)



(**23**)



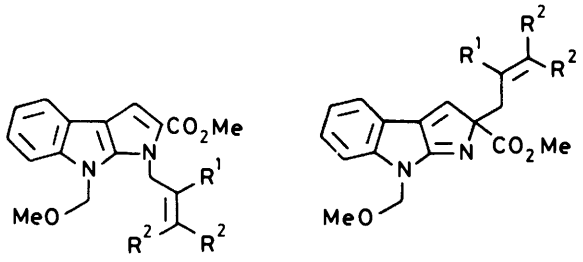
(2)

2*H*-Pyrroles can also be formed directly by treatment of pyrrolylmagnesium halides with alkylating agents. However, formation of pyrroloindolylmagnesium bromides by reaction of the pyrroloindoles with ethylmagnesium bromide, followed by addition of iodomethane resulted only in the recovery of starting material. This is in contrast to the reaction of the sodium derivative of the pyrroloindole (**6d**) with allyl bromide which does lead to the 2*H*-isomer (**23**) albeit as the minor product, as already described.

Reaction of the sodium derivative of (**6d**) with methylallyl chloride gave the *N*-methylallyl derivative (**24a**) (72%) together with the 2*H*-isomer (**25a**) (11%). Reaction with prenyl

* Determined by Dr. D. J. Williams of this department.

bromide,* however, resulted in the formation of the 2*H*-isomer (**25b**) as the major product (41%), together with the *N*-prenyl derivative (**24b**) (6%). When the potassium derivative of the pyrroloindole (**6d**) was treated with prenyl bromide, the ratio of N- to C-alkylation was increased, and the 2*H*-isomer (**25b**) (56%) and the *N*-prenyl derivative (**24b**) (18%) were obtained. This is in accord with the chemistry of simple pyrroles, where the potassium derivatives are known to show a higher tendency towards N-alkylation.[17] The reason for the great difference in the ratio of N to C alkylation between prenyl bromide and allyl bromide is not clear. On irradiation in cyclohexane, the *N*-substituted derivatives (**24**) underwent rearrangement to the 2*H*-isomers (**25**), the prenyl group migrating without allylic inversion.



(**24**) (**25**)

a; R^1 = Me, R^2 = H
b; R^1 = H, R^2 = Me

Therefore the attempts to introduce the 3a-substituent into the pyrroloindole by transfer of allyl groups from nitrogen to carbon were frustrated by the preferred migration to the 2-position. It is possible that this unwanted rearrangement might be suppressed by prior reduction of the 2,3-double bond.

Experimental

U.v. spectra were recorded on a Pye Unicam SP800 spectrophotometer. ^{13}C N.m.r. spectra were recorded using a Bruker WM250 spectrometer operating at 62.9 MHz, and were broad band decoupled. Photochemical reactions were carried out in quartz vessels in a Rayonet photochemical reactor. For other general points see ref. 1.

1-Methylindole-3-carbaldehyde (**1a**).—This was prepared (65%) by alkylation of indole-3-carbaldehyde using iodomethane with potassium carbonate as base in acetone, m.p. 65—68 °C (lit.,[18] m.p. 67 °C).

1-Benzylindole-3-carbaldehyde (**1b**).—This compound was prepared (79%) by alkylation of indole-3-carbaldehyde using benzyl bromide with potassium carbonate as base in acetone, m.p. 108—109 °C (lit.,[19] m.p. 102—104 °C).

1-Methoxymethylindole-3-carbaldehyde (**1c**).—This compound was prepared (86%) by alkylation of indole-3-carbaldehyde using chloromethyl methyl ether with sodium hydride as base in dimethylformamide, m.p. 77—78 °C (Found: C, 69.8; H, 5.9; N, 7.4. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.9; N, 7.4%); $\nu_{max.}$ 1 640 cm^{-1}; δ (90 MHz, $CDCl_3$) 3.27 (3 H, s), 5.48 (2 H, s), 7.25—7.60 (3 H, m), 7.79 (1 H, s), 8.31 (1 H, m), and 10.00 (1 H, s).

* Prenyl = 3-methylbut-2-enyl

Ethyl 2-Azido-3-(1-methylindol-3-yl)propenoate (**2a**).—A solution of 1-methylindole-3-carbaldehyde (**1a**) (1.00 g, 6.28 mmol) in ethyl azidoacetate (3.24 g, 25.16 mmol) was added dropwise to a stirred solution of sodium (0.58 g, 25.16 mg atom) in ethanol (12 ml) at −15 °C. The mixture was maintained between −15 and −5 °C for 6 h, allowed to warm to room temperature, and then poured into saturated aqueous ammonium chloride and extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), evaporated, and the residue chromatographed to give the *title azide* (**2a**) (1.16 g, 62%), m.p. 100—102 °C, $\nu_{max.}$ 2 110, 2 090, 1 693, and 1 611 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.39 (3 H, t), 3.82 (3 H, s), 4.39 (2 H, q), 7.33 (4 H, m), 7.78 (1 H, m), and 8.04 (1 H, s); *m/z* 270 (M^+, base), 242, and 196.

Ethyl 2-Azido-3-(1-benzylindol-3-yl)propenoate (**2b**).—A solution of 1-benzylindole-3-carbaldehyde (**1b**) (1.00 g, 4.26 mmol) and ethyl azidoacetate (2.20 g, 17.02 mmol) in tetrahydrofuran (3 ml) was added dropwise to a stirred solution of sodium (0.391 g, 17.02 mg-atom) in ethanol (10 ml) at −15 °C. The remainder of the process was as described above, chromatography of the crude product giving the *title azide* (**2b**) (0.455 g, 31%), m.p. 85—89 °C (decomp.); $\nu_{max.}$ 2 110, 1 690, 1 650, and 1 615 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.39 (3 H, t), 4.40 (2 H, q), 5.40 (2 H, s), 7.30 (9 H, m), 7.83 (1 H, m), and 8.18 (1 H, s); *m/z* 346 (M^+), 318, 272, 245, and 91 (base).

Ethyl 2-Azido-3-(1-methoxymethylindol-3-yl)propenoate (**2c**).—A solution of 1-methoxymethylindole-3-carbaldehyde (**1c**) (1.00 g, 5.29 mmol) in ethyl azidoacetate (2.73 g, 21.16 mmol) was added dropwise to a stirred solution of sodium (0.49 g, 21.16 mg-atom) in ethanol (14 ml) at −15 °C. Work-up as above, and chromatography of the crude product gave the *title azide* (**2c**) (1.29 g, 81%), m.p. 90—92.5 °C (decomp.); $\nu_{max.}$ 2 120, 1 690, and 1 611 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.40 (3 H, t), 3.27 (3 H, s), 4.40 (2 H, q), 5.51 (2 H, s), 7.25—7.40 (2 H, m), 7.32 (1 H, s), 7.55 (1 H, m), 7.79 (1 H, m), and 8.16 (1 H, s); *m/z* 300 (M^+) 272 (base), 241, 227, 199, 196, 195, 181, 168, 153, 140, and 127.

Methyl 2-Azido-3-(1-methoxymethylindol-3-yl)propenoate (**2d**).—A solution of 1-methoxymethylindole-3-carbaldehyde (**1c**) (6.08 g, 32.17 mmol) in methyl azidoacetate (14.80 g, 128.7 mmol) was added dropwise to a stirred solution of sodium (2.96 g, 128.7 mg atom) in methanol (100 ml) at −15 °C. Work-up as above, and chromatography gave the *title azide* (**2d**) (5.50 g, 60%) as yellow needles, m.p. 113.5—116 °C (from methanol) (Found: C, 58.5; H, 4.9; N, 19.5. $C_{14}H_{14}N_4O_3$ requires C, 58.7; H, 4.9; N, 19.6%); $\nu_{max.}$ 2 140, 1 697, 1 618, and 1 609 cm^{-1}; δ (90 MHz, $CDCl_3$) 3.30 (3 H, s), 3.92 (3 H, s), 5.48 (2 H, s), 7.20—7.35 (2 H, m), 7.27 (1 H, s), 7.48 (1 H, m), 7.73 (1 H, m), and 8.10 (1 H, s); *m/z* 286 (M^+), 258 (base), 226, 196, 195, 181, and 168.

3-Azidoacetylindole (**4a**).—A mixture of 3-chloroacetylindole[5] (**3**) (300 mg, 1.55 mmol) and sodium azide (202 mg, 3.10 mmol) was heated overnight in a refluxing mixture of acetone (20 ml) and water (10 ml). The resulting solution was diluted with water and extracted with dichloromethane. The combined organic extract was dried ($MgSO_4$) and evaporated to give a quantitative yield of the *title compound* (**4a**) as a pale yellow solid, m.p. 172.5—175 °C (decomp.) (Found: C, 59.8; H, 4.0; N, 27.7; $C_{10}H_8N_4O$ requires C, 60.0; H, 4.0; N, 28.0%); $\nu_{max.}$ 3 320, 2 103, and 1 637 cm^{-1}; δ [90 MHz, $CDCl_3$–$(CD_3)_2SO$] 4.39 (2 H, s), 7.12 (2 H, m), 7.35 (1 H, m), 7.89 (1 H, d), 8.12 (1 H, m), and 11.78 (1 H, br); *m/z* 200 (M^+), 172, 144 (base), 106, and 89.

3-Azidoacetyl-1-methylindole (**4b**).—A mixture of the indole (**4a**) (0.892 g, 4.46 mmol), potassium carbonate (3.00 g, 21.7 mmol), and an excess of iodomethane (*ca.* 10 equiv.) was heated

under reflux in acetone for 16 h. The mixture was filtered and evaporated to leave a red gum, which was purified to a yellow oil by filtration through a pad of silica gel with ether as eluant. The oil solidified on cooling and recrystallisation from ethanol–light petroleum gave the *title compound* (**4b**) (0.787 g, 82%), m.p. 77—78.5 °C (Found: C, 61.7; H, 4.6; N, 26.1. $C_{11}H_{10}N_4O$ requires C, 61.7; H, 4.7; N, 26.15%); $\nu_{max.}$ 2 100 and 1 660 cm^{-1}; δ (90 MHz, $CDCl_3$) 3.76 (3 H, s), 4.21 (2 H, s), 7.30 (3 H, m), 7.53 (1 H, s), and 8.26 (1 H, m); *m/z* 214 (M^+), 186, and 158 (base).

(E/Z)-1-*Azido*-2-*indol*-3-*ylethene* (**5a**).—The azido ketone (**4a**) (200 mg, 1 mmol) was dissolved in ethanol (40 ml) and treated with an excess of sodium borohydride and glacial acetic acid (10 drops) at room temperature. After 2 h the mixture was poured into brine and extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4) and evaporated to give 2-*azido*-1-*indol*-3-*ylethanol* as a yellow gum (180 mg, 89%), $\nu_{max.}$ 3 510, 3 410, and 2 102 cm^{-1}. The azido alcohol (180 mg, 0.89 mmol) was dissolved in dichloromethane (20 ml), and stirred in ice whilst methanesulphonyl chloride (90 μl, 1.16 mmol) was added. After 5 min, triethylamine (0.39 ml, 2.8 mmol) was added, and the mixture stirred for a further 1 h. The mixture was poured onto ice–water and extracted with ether. The combined extracts were dried (Na_2SO_4) and evaporated to a brown oil, which was chromatographed on alumina to give the *title azide* (**5a**) (82 mg, 50%) as an unstable yellow oil which darkened rapidly, $\nu_{max.}$ 3 400, 2 110, and 1 630 cm^{-1}; δ (90 MHz, $CDCl_3$) 6.12 (2 H, AB quartet, *J* 7.4 Hz, *Z*-isomer), 6.56 (2 H, AB quartet, *J* 14 Hz, *E*-isomer), 7.0—7.4 (m), 7.45—7.65 (m), and 7.9 (br s).

(E/Z)-1-*Azido*-2-(1-*methylindol*-3-*yl*)*ethene* (**5b**).—The azido ketone (**4b**) (300 mg, 1.4 mmol) was reduced with sodium borohydride as described above to give 2-*azido*-1-(1-*methylindol*-3-*yl*)*ethanol* (290 mg, 96%) as a yellow gum, $\nu_{max.}$ 3 410 and 2 100 cm^{-1}. This azido alcohol (290 mg, 1.34 mmol) was dissolved in dichloromethane (5 ml), and treated with methanesulphonyl chloride (125 μl, 1.62 mmol) and triethylamine (0.56 ml, 4.02 mmol) as described above. Work-up and chromatography gave the *title azide* (**5b**) (242 mg, 92%) as a yellow oil which darkened rapidly, $\nu_{max.}$ 2 110 and 1 631 cm^{-1}; δ (90 MHz, $CDCl_3$) *Z*-isomer, 3.63 (3 H, s), 6.02 (2 H, AB quartet *J* 8 Hz), and 7.00—7.70 (m); *E*-isomer, 3.54 (3 H, s), 6.44 (2 H, AB quartet, *J* 15 Hz), and 7.00—7.70 (m).

Thermolysis of the Azide (**2a**).—A solution of the azide (**2a**) (1.174 g) in toluene (235 ml) was added dropwise to refluxing toluene (235 ml) over 1 h. The solution was refluxed for a further 10 min, and then evaporated to a brown solid which was dissolved in ether and purified by filtration through silica gel. Evaporation of the filtrate gave *ethyl* 1,8-*dihydro*-8-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**6a**) (0.987 g, 94%) as colourless crystals, m.p. 234—239 °C (decomp.) (Found: C, 69.25; H, 5.85; N, 11.3. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N, 11.6%); $\nu_{max.}$ 3 240, 1 665, and 1 625 cm^{-1}; $\lambda_{max.}$ (EtOH) 279 (log ε 4.35) and 336 nm (4.55); δ [90 MHz, $(CD_3)_2SO$] 1.31 (3 H, t), 3.81 (3 H, s), 4.30 (2 H, q), 7.15 (2 H, m), 7.17 (1 H, s), 7.40 (1 H, m), and 7.65 (1 H, m), NH not observed; *m/z* 242 (M^+), 196 (base), 168, and 127.

Thermolysis of the Azide (**2b**).—A solution of the azide (**2b**) (0.50 g) in toluene (100 ml) was added dropwise to refluxing toluene (100 ml). The solution was refluxed for a further 10 min, and then evaporated to leave a brown solid. Trituration with light petroleum–ether (4:1) gave *ethyl* 8-*benzyl*-1,8-*dihydropyrrolo*[2,3-b]*indole*-2-*carboxylate* (**6b**) (0.419 g, 91%) as a yellow solid, m.p. 217—218 °C (Found: C, 75.3; H, 5.8; N, 8.7. $C_{20}H_{18}N_2O_2$ requires C, 75.5; H, 5.7; N, 8.8%); $\nu_{max.}$ 3 275, 1 663, 1 630, and 1 598 cm^{-1}; δ [90 MHz, $CDCl_3$–$(CD_3)_2SO$] 1.33 (3 H, t), 4.30 (2 H, q), 5.48 (2 H, s), 7.20 (9 H, m), and 7.67 (1 H, m), NH not observed; *m/z* 318 (M^+), 272, and 91 (base).

Thermolysis of the Azide (**2c**).—A solution of the azide (**2c**) (1.144 g) in toluene (230 ml) was added dropwise during 80 min to refluxing toluene (230 ml). Evaporation of the toluene and crystallisation of the residue from ethanol gave *ethyl* 1,8-*dihydro*-8-*methoxymethylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**6c**) (0.828 g, 80%) as needles, m.p. 173—180 °C (Found: C, 66.2; H, 6.0; N, 10.3. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ 3 250, 1 650, 1 615, and 1 579 cm^{-1}; δ [90 MHz, $(CD_3)_2SO$] 1.30 (3 H, t), 3.23 (3 H, s), 4.32 (2 H, q), 5.72 (2 H, s), 7.10—7.30 (2 H, m), 7.21 (1 H, s), 7.55 (1 H, m), 7.71 (1 H, m), and 12.20 (1 H, br s); *m/z* 272 (M^+, base), 226, 195, and 168.

Thermolysis of the Azide (**2d**).—A solution of the azide (**2d**) (7.50 g) in toluene (500 ml) was added dropwise to refluxing toluene (500 ml) over 1 h. The solution was refluxed for a further 0.5 h and then concentrated to 100 ml. On cooling, *methyl* 1,8-*dihydro*-8-*methoxymethylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**6d**) (4.72 g, 70%) crystallised as colourless needles, m.p. 214—218 °C (decomp.) (Found: C, 64.9; H, 5.4; N, 10.8. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.85%); $\nu_{max.}$ 3 300, 3 260, 1 662, 1 620, and 1 588 cm^{-1}; δ (250 MHz, $CDCl_3$) 3.32 (3 H, s), 3.94 (3 H, s), 5.60 (2 H, s), 7.23 (2 H, m), 7.26 (1 H, s), 7.41 (1 H, m), 7.73 (1 H, m), and 9.87 (1 H, br s); *m/z* 258 (M^+, base), 227, 195, and 168.

Thermolysis of the Azide (**5b**).—A solution of the azide (**5b**) (50 mg) in toluene (10 ml) was heated under reflux for 5 min. The resulting dark solution was evaporated to a gum, the major component of which was tentatively assigned as 1,8-*dihydro*-8-*methylpyrrolo*[2,3-b]*indole* (**7**), δ (90 MHz, $CDCl_3$), 3.49 (3 H, s), and 6.44 (2 H, AB quartet, *J* 3 Hz) *inter alia*.

Deprotection of the Pyrroloindole (**6d**).—The pyrroloindole (**6d**) (100 mg) was dissolved in a mixture of methanol (40 ml), water (6 ml), and hydrochloric acid (1.4M; 4 ml), and the solution was kept at room temperature for 7 days. More hydrochloric acid (2.4M; 12 ml) was added, and after a further 7 days, the solution was neutralised with sodium hydrogen carbonate. The methanol was evaporated off, and the residual aqueous solution was extracted with ethyl acetate. The organic extracts were dried ($MgSO_4$), evaporated, and the residue chromatographed to give (i) recovered pyrroloindole (**6d**) (4 mg, 4%) and (ii) methyl 1,8-dihydropyrrolo[2,3-*b*]indole-2-carboxylate (**11**) (33 mg, 40%), m.p. 230—236 °C (lit.,[9a] 229—231 °C) (Found: C, 67.1; H, 4.7; N, 12.9. $C_{12}H_{10}N_2O_2$ requires C, 67.3; H, 4.7; N, 13.1%); $\nu_{max.}$ 3 370, 3 280, and 1 655 cm^{-1}; δ [250 MHz, $(CD_3)_2SO$] 3.78 (3 H, s), 7.06 (2 H, m), 7.13 (1 H, s), 7.33 (1 H, m), 7.62 (1 H, m), 11.11 (1 H, br), and 11.90 (1 H, br); *m/z* 214 (M^+), 182 (base), 154, and 127.

Methyl 1,8-*Dihydro*-8-*methoxymethyl*-1-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**12**).—A solution of the pyrroloindole (**6d**) (1.00 g, 3.88 mmol) in dimethylformamide (10 ml) was added to a stirred suspension of sodium hydride (50%; 0.466 g, 9.71 mmol) in dimethylformamide (5 ml). The mixture was stirred at 70 °C for 2 h, and then iodomethane (0.40 ml) was added. After a further 0.5 h the mixture was poured into water and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to a gum. Trituration with light petroleum gave the *title compound* (**12**) (0.882 g, 84%) as a solid, m.p. 106—107.5 °C (from methanol) (Found: C, 66.1; H, 5.9; N, 10.3. $C_{15}H_{16}N_2O_3$ requires C, 66.2; H, 5.9; N, 10.3%); $\nu_{max.}$ 1 704 cm^{-1}; δ (250 MHz, $CDCl_3$) 3.30 (3 H, s), 3.84 (3 H, s), 4.23 (3 H, s), 5.56 (2 H, s), 7.20 (2 H, m), 7.29 (1 H, s), 7.37 (1 H, m), and 7.67

(1 H, m); δ_C($CDCl_3$) 32.9, 50.7, 55.8, 74.4, 108.9, 109.2, 109.3, 119.4, 120.8, 121.6, 121.8, 122.1, 142.7, 143.8, and 162.2; *m/z* 272 (M^+), 242, and 227 (base).

Deprotection of Pyrroloindole (**12**).—A solution of the pyrroloindole (**12**) (0.75 g) in methanol (225 ml) and water (75 ml) was treated with hydrochloric acid (2.4M; 30 ml), and the solution kept at room temperature for 5 days. The solution was neutralised with sodium hydrogen carbonate and extracted with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and evaporated to give a brown solid. The solid was dissolved in ether and filtered through a pad of silica gel. Evaporation of the filtrate gave *methyl* 1,8-*dihydro*-1-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**13**) (0.575 g, 91%) as a buff powder, m.p. 185—190 °C (decomp.) (Found: C, 68.1; H, 5.3; N, 12.1. $C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.3; N, 12.3%); $\nu_{max.}$ 3 230 and 1 645 cm^{-1}; δ [250 MHz, $(CD_3)_2SO$] 3.74 (3 H, s), 3.96 (3 H, s), 7.09 (2 H, m), 7.21 (1 H, s), 7.36 (1 H, m), 7.64 (1 H, m), and 11.41 (1 H, br); *m/z* 228 (M^+, base), 197, and 170.

Hydrolysis of the Pyrroloindole (**12**).—The pyrroloindole (**12**) (392 mg) was dissolved in a mixture of methanol (50 ml), water (17 ml), and sodium hydroxide solution (1M; 8 ml), and the resulting solution heated on a steam-bath for 2.5 h. After cooling, the solution was acidified to pH 6, and extracted with ethyl acetate. The combined extracts were dried ($MgSO_4$) and evaporated to leave a pale blue oily solid. Washing of this with hot light petroleum left 1,8-*dihydro*-8-*methoxymethyl*-1-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylic acid* (**14**) (166 mg, 45%) as a pale blue solid which was recrystallised from methanol–nitromethane, m.p. 124—126 °C (decomp.) (Found: M^+, 258.1010. $C_{14}H_{14}N_2O_3$ requires M^+, 258.1004); $\nu_{max.}$ 2 560—3 120 and 1 665 cm^{-1}; δ [90 MHz, $(CD_3)_2SO$] 3.21 (3 H, s), 4.16 (3 H, s), 5.71 (2 H, s), 7.16 (2 H, m), 7.19 (1 H, s), and 7.60 (2 H, m); *m/z* 258 (M^+), 214, and 169 (base). The petroleum washings were chromatographed to give 1,8-*dihydro*-8-*methoxymethyl*-1-*methylpyrrolo*[2,3-b]*indole* (**15**) (75 mg, 24%) as an unstable colourless oil (Found: M^+, 214.1110. $C_{13}H_{14}N_2O$ requires M^+, 214.1106); δ [250 MHz, $(CD_3)_2CO$] 3.23 (3 H, s), 3.91 (3 H, s), 5.69 (2 H, s), 6.31 (1 H, d, *J* 3.1 Hz), 6.54 (1 H, d, 3.1 Hz), 7.06 (2 H, m), and 7.54 (2 H, m).

Reduction of the Pyrroloindole (**12**).—(a) *With lithium aluminium hydride*. A solution of the pyrroloindole (**12**) (228 mg, 0.84 mmol) in tetrahydrofuran (7 ml) was added to a suspension of lithium aluminium hydride (64 mg, 1.68 mmol) in tetrahydrofuran. The reaction mixture was stirred at room temperature overnight. Work-up and chromatography of the crude product gave *bis*(1,8-*dihydro*-8-*methoxymethyl*-1-*methylpyrrolo*[2,3-b]*indolyl*)*methane* (**16**) (81 mg, 44%), m.p. 220—225 °C (decomp.) (Found: C, 73.6; H, 6.3; N, 12.8. $C_{27}H_{28}N_4O_2$ requires C, 73.6; H, 6.4; N, 12.7%); δ [250 MHz, $CDCl_3$–$(CD_3)_2SO$] 3.26 (6 H, s), 3.86 (6 H, s), 4.18 (2 H, s), 5.67 (4 H, s), 6.12 (2 H, s), 7.05 (4 H, m), and 7.48 (4 H, m); *m/z* 440 (M^+, base), and 395.

(b) *With sodium cyanoborohydride*. Excess of sodium cyanoborohydride was added to a solution of the pyrroloindole (**12**) (100 mg) in glacial acetic acid (10 ml). The mixture was heated at 60—70 °C for 4 h, and then poured into water, neutralised with sodium hydrogen carbonate, and extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), and evaporated to give *methyl* 1,8-*dihydro*-1,8-*dimethylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**18**) (78 mg, 88%), m.p. 133.5—136 °C (Found: C, 69.4; H, 5.8; N, 11.5. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N, 11.6%); $\nu_{max.}$ 1 690 cm^{-1}; δ (90 MHz, $CDCl_3$) 3.88 (6 H, s), 4.23 (3 H, s), 7.25 (3 H, m), 7.30 (1 H, s), and 7.67 (1 H, m); *m/z* 242 (M^+, base) and 221.

(c) *With 'copper*(I) *hydride'*. A toluene solution of sodium bis(2-methoxyethoxy)aluminium hydride (3.5M; 3.4 ml, 11.9 mmol) was added to a stirred suspension of copper(I) bromide (832 mg, 5.8 mmol) in tetrahydrofuran at 0 °C under nitrogen. After being stirred for 0.5 h at 0 °C, the mixture was cooled to −78 °C, and treated successively with butan-2-ol (1.0 ml, 10.9 mmol) and a solution of the pyrroloindole (**12**) (150 mg, 0.55 mmol) in tetrahydrofuran (5 ml). The mixture was stirred for 2 h at −78 °C, and then for 4 h at room temperature. Aqueous work-up and chromatography gave (i) 1,8-*dihydro*-1,2-*dimethyl*-8-*methoxymethylpyrrolo*[2,3-b]*indole* (**19**) (22 mg, 17%) (Found: M^+, 228.1263. $C_{14}H_{16}N_2O$ requires M^+, 228.1263); δ (90 MHz, $CDCl_3$) 2.39 (3 H, d, *J* 1.0 Hz), 3.27 (3 H, s), 3.78 (3 H, s), 5.57 (2 H, s), 6.20 (1 H, d, *J* 1.0 Hz), 7.16 (2 H, m), 7.35 (1 H, m), and 7.59 (1 H, m); *m/z* 228 (M^+), 197, and 183 (base); (ii) starting pyrroloindole (**12**) (26 mg, 17%), and (iii) the bis(pyrroloindolyl)methane (**16**) (20 mg, 16%).

Reduction of the Pyrroloindole (**6d**).—Concentrated hydrochloric acid (10 drops) was added to a stirred mixture of the pyrroloindole (**6d**) (100 mg, 0.39 mmol) and borane–trimethylamine (113 mg, 1.55 mmol) in dioxane (10 ml). The mixture was heated under reflux for 0.5 h, concentrated, and the residue was partitioned between aqueous sodium hydrogen carbonate and ether. The ether layer was dried ($MgSO_4$), evaporated, and the residue chromatographed to give *methyl* 1,8-*dihydro*-8-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**17**) (28 mg, 32%), $\nu_{max.}$ 3 280 and 1 652 cm^{-1}; δ [250 MHz, $CDCl_3$–$(CD_3)_2SO$] 3.80 (3 H, s), 3.81 (3 H, s), 7.13 (2 H, m), 7.15 (1 H, s), 7.39 (1 H, m), 7.66 (1 H, m), and 10.81 (1 H, br); *m/z* 228 (M^+), 196 (base), and 168.

Methyl 8-*Allyl*-1,8-*dihydro*-1-*methylpyrrolo*[2,3-b]*indole*-2-*carboxylate* (**20**).—The pyrroloindole (**13**) (250 mg, 1.38 mmol) was dissolved in dimethylformamide (5 ml) and added to a suspension of sodium hydride (50%; 158 mg, 3.29 mmol) in dimethylformamide (5 ml). The mixture was stirred at room temperature for 1 h, and then allyl bromide (180 μl, 2.07 mmol) was added. After stirring for a further 1 h, work-up and chromatography gave the *title compound* (**20**) (284 mg, 97%), m.p. 85—87 °C (from petroleum) (Found: C, 71.8; H, 6.1; N, 10.4. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.0; N, 10.4%); $\nu_{max.}$ 1 703 cm^{-1}; δ (250 MHz, $CDCl_3$) 3.83 (3 H, s), 4.16 (3 H, s), 4.89 (2 H, m), 4.97 (1 H, d, *J* 17 Hz with additional splitting), 5.20 (1 H, d, *J* 10.5 Hz with additional splitting), 6.04 (1 H, m), 7.17 (3 H, m), 7.31 (1 H, s), and 7.69 (1 H, m); *m/z* 268 (M^+) and 227 (base).

Methyl 1-*Allyl*-1,8-*dihydro*-8-*methoxymethylpyrrolo*[2,3-b]-*indole*-2-*carboxylate* (**21**).—The pyrroloindole (**6d**) (500 mg, 1.94 mmol) was treated with sodium hydride (50%; 280 mg, 5.82 mmol) and allyl bromide (252 μl, 2.91 mmol) in dimethylformamide (10 ml) exactly as described for compound (**20**). Work-up and chromatography gave (i) the *title compound* (**21**) (410 mg, 71%) as a gum, $\nu_{max.}$ 1 692 cm^{-1}; $\lambda_{max.}$ (MeOH) 232, 272, 321sh, and 327 nm; δ (250 MHz, $CDCl_3$), 3.29 (3 H, s), 3.84 (3 H, s), 4.79 (1 H, d, *J* 16.7 Hz with additional splitting), 5.13 (1 H, d, *J* 10.6 Hz with additional splitting), 5.40 (2 H, m), 5.47 (2 H, s), 6.14 (1 H, m), 7.22 (2 H, m), 7.38 (1 H, m), 7.39 (1 H, s), and 7.71 (1 H, m); δ_C($CDCl_3$) 47.6, 50.7, 55.8, 74.4, 109.2, 109.4, 115.1, 119.4, 120.8, 121.1, 121.5, 122.2, 135.5, 142.6, 143.5, and 161.9, only 16 distinct lines; *m/z* 298 (M^+, base) and 253; *picrate*, m.p. 87—90 °C (Found: C, 52.6; H, 4.0; N, 13.25. $C_{23}H_{21}N_5O_{10}$ requires C, 52.4; H, 4.0; N, 13.3%), and (ii) the 2*H*-pyrroloindole (**23**) (75 mg, 13%), data given below.

Irradiation of the 1-*Allylpyrroloindole* (**21**).—A solution of the pyrroloindole (**21**) (310 mg) in cyclohexane (200 ml) was irradiated at 300 nm for 40 min. The solvent was evaporated and the residue chromatographed to give (i) the pyrroloindole (**6d**) (29 mg, 11%) and (ii) *methyl* 2-*allyl*-2,8-*dihydro*-8-*methoxy*-

methyl-2H-*pyrrolo*[2,3-b]*indole*-2-*carboxylate* (**23**) (192 mg, 62%), m.p. 87—89 °C (Found: C, 68.5; H, 6.1; N, 9.3. $C_{17}H_{18}N_2O_3$ requires C, 68.4; H, 6.1; N, 9.4%); $\nu_{max.}$ 1 730 cm^{-1}; $\lambda_{max.}$ (MeOH) 248sh (log ε 4.34), 253 (4.38), 278 (3.44), and 290 nm (3.39); δ (250 MHz, $CDCl_3$) 2.93 (2 H, m), 3.38 (3 H, s), 3.70 (3 H, s), 5.02 (1 H, d, *J* 10 Hz with additional splitting), 5.12 (1 H, d, *J* 16.9 Hz with additional splitting), 5.31 (2 H, AB q, *J* 11.5 Hz), 5.68 (1 H, m), 7.08 (2 H, m), 7.15 (1 H, s), 7.35 (1 H, m), and 7.56 (1 H, m); δ_C ($CDCl_3$) 39.7, 52.4, 56.3, 73.6, 92.95, 110.5, 118.5, 118.6, 121.7, 124.6, 130.3, 132.5, 135.2, 139.2, 151.7, 170.9, and 172.3; *m/z* 298 (M^+, base), 257, 253, 239, 227, and 207.

Methyl 1,8-*Dihydro*-8-*methoxymethyl*-1-(2-*methylallyl*)*pyrrolo*[2,3-b]*indole*-2-*carboxylate* (**24a**).—The pyrroloindole (**6d**) (500 mg, 1.94 mmol) was treated with sodium hydride (50%; 140 mg, 2.91 mmol) and 3-chloro-2-methylprop-1-ene (284 μl, 2.91 mmol) in dimethylformamide (10 ml) exactly as described for compound (**20**). Work-up and chromatography gave (i) the *title compound* (**24a**) (436 mg, 72%) as a gum, $\nu_{max.}$ 1 690 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.86 (3 H, br s), 3.30 (3 H, s), 3.83 (3 H, s), 4.20 (1 H, br s), 4.80 (1 H, br s), 5.29 (2 H, br s), 5.44 (2 H, s), 7.21 (2 H, m), 7.37 (1 H, s), 7.38 (1 H, m), and 7.71 (1 H, m); δ_C ($CDCl_3$) 19.7, 50.4, 50.7, 55.7, 74.3, 109.18, 109.22, 109.3, 119.4, 120.7, 121.1, 121.4, 122.2, 142.5, 143.4, 143.6, and 161.9; *m/z* 312 (M^+, base), 227, 221, and 207; *picrate* m.p. 78—80 °C (Found: C, 53.5; H, 4.2; N, 12.9. $C_{24}H_{23}N_5O_{10}$ requires C, 53.2; H, 4.3; N, 12.9%); (ii) unchanged pyrroloindole (**6d**) (54 mg, 11%); and (iii) the 2*H*-pyrroloindole (**25a**) (64 mg, 11%), data given below.

Irradiation of the 1-(2-*Methylallyl*)*pyrroloindole* (**24a**).—A solution of the pyrroloindole (**24a**) (200 mg) in cyclohexane (200 ml) was irradiated at 300 nm for 40 min. Evaporation of the solvent, and chromatography of the residue gave (i) the pyrroloindole (**6d**) (25 mg, 15%); and (ii) *methyl* 2,8-*dihydro*-8-*methoxymethyl*-2-(2-*methylallyl*)-2H-*pyrrolo*[2,3-b]*indole*-2-*carboxylate* (**25a**) (99 mg, 50%) as a yellow gum (Found: M^+, 312.1478. $C_{18}H_{20}N_2O_3$ requires M^+, 312.1474); $\nu_{max.}$ 1730 cm^{-1}; $\lambda_{max.}$ (MeOH) 248sh, 252, 275, and 290 nm; δ (250 MHz, $CDCl_3$), 1.75 (3 H, br s), 2.89 (2 H, br s), 3.38 (3 H, s), 3.70 (3 H, s), 4.70—4.84 (2 H, m), 5.30 (2 H, ABq, *J* 11 Hz), 7.07 (2 H, m), 7.18 (1 H, s), 7.34 (1 H, m), and 7.56 (1 H, m); δ_C ($CDCl_3$) 24.1, 43.3, 52.4, 56.2, 73.6, 93.4, 110.5, 114.9, 118.7, 121.7, 124.5, 130.3, 134.6, 139.6, 140.8, 151.7, 171.1, and 171.9; *m/z* 312 (M^+, base), 227, and 221.

Methyl 1,8-*Dihydro*-1-(1,1-*dimethylallyl*)-8-*methoxymethyl*-*pyrrolo*[2,3-b]*indole*-2-*carboxylate* (**24b**) *and Methyl* 2,8-*Dihydro*-2-(1,1-*dimethylallyl*)-8-*methoxymethyl*-2H-*pyrrolo*-[2,3-b]*indole*-2-*carboxylate* (**25b**).—(a) The pyrroloindole (**6d**) (500 mg, 1.94 mmol) was treated with sodium hydride (50%; 97 mg, 2.02 mmol) and 1,1-dimethylallyl bromide (230 μl, 2.33 mmol) in dimethylformamide (10 ml) exactly as described for compound (**20**). Work-up and chromatography gave (i) the *pyrroloindole* (**24b**) (37 mg, 6%) as an oil, $\nu_{max.}$ 1 695 cm^{-1}, δ (250 MHz, $CDCl_3$) 1.70 (3 H, d, *J* 1.8 Hz), 1.80 (3 H, d, *J* 1.2 Hz), 3.29 (3 H, s), 3.84 (3 H, s), 5.27 (1 H, m), 5.38 (2 H, m), 5.51 (2 H, s), 7.70 (2 H, m), 7.33 (1 H, s), 7.39 (1 H, m), and 7.68 (1 H, m); *m/z* 326 (M^+, base); (ii) unchanged pyrroloindole (**6d**) (64 mg, 13%); (iii) a 1:1 mixture of (**6d**) and (**25b**), and (iv) the 2H-*pyrroloindole* (**25b**) (260 mg, 41%) as a gum (Found: M^+, 326.1626. $C_{19}H_{22}N_2O_3$ requires M^+, 326.1630); $\nu_{max.}$ 1 730 cm^{-1}; $\lambda_{max.}$ (MeOH) 247sh (log ε 4.41), 252 (4.44), 276 (3.67), and 290 nm (3.57); δ (250 MHz, $CDCl_3$), 1.64 (6 H, br s), 2.86 (2 H, m), 3.36 (3 H, s), 3.69 (3 H, s), 5.06 (1 H, br t), 5.30 (2 H, AB q, *J* 11.2 Hz), 7.08 (2 H, m), 7.17 (1 H, s), 7.33 (1 H, m), and 7.61 (1 H, m); δ_C ($CDCl_3$) 17.8, 25.7, 34.4, 52.2, 56.1, 73.6, 93.7, 110.5, 118.4, 118.8, 121.6, 124.4, 130.2, 134.7, 134.9, 139.6, 151.7, 171.2, and 172.0; *m/z* 326 (M^+), 295, 258 (base), 227, and 226.

(b) The pyrroloindole (**6d**) (245 mg, 0.95 mmol) was treated with potassium hydride (25%; 167 mg, 1.04 mmol) and 1,1-dimethylallyl bromide (115 μl, 2.16 mmol) exactly as described in (a) to give after chromatography, the pyrroloindole (**24b**) (56 mg, 18%), and the 2*H*-pyrroloindole (**25b**) (175 mg, 56%).

Irradiation of the 1-(1,1-*Dimethylallyl*)*pyrroloindole* (**24b**).—A solution of the pyrroloindole (**24b**) (10 mg) in cyclohexane (20 ml) was irradiated at 254 nm for 15 min. The solvent was evaporated, and the residue was shown by t.l.c. and n.m.r. spectroscopy (250 MHz) to consist of the 2*H*-pyrroloindole (**25b**).

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