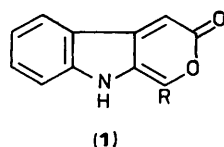# Diels–Alder Reactivity of Pyrano[3,4-b]indol-3-ones. Part 2.[1] Steric and Electronic Effects in the Addition to Alkynes

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The pyrano[3,4-b]indol-3-ones (1a), prepared from ethyl 2-acetoxymethylindol-3-ylacetate (2), and (1b)—(1h), prepared from indol-3-ylacetic acid, undergo Diels–Alder reaction with dimethyl acetylenedicarboxylate to give, with concomitant loss of carbon dioxide, carbazole 2,3-diesters (7). The reactions of (1) with the unsymmetrical acetylene, ethyl propiolate, give mixtures of the carbazole 3-ester (8) and carbazole 2-ester (9), with the former predominating. The regioselectivity of the Diels–Alder reaction increases with increasing steric bulk at the 1-position of the dienes (1), although in the case of the N-ethoxycarbonyl derivative (10) regioselectivity is reversed. Reaction of the pyrone (1b) with a variety of unsymmetrical acetylenes gives mixtures of carbazoles (13) and (14), the regioselectivity of the Diels–Alder reaction being dependent on the acetylene substituents, and in some cases being regiospecific.

The Diels–Alder reaction of indole-2,3-quinodimethanes has been the subject of considerable interest in the last few years.[2,3] We have recently reported that the pyrano[3,4-b]indol-3-one (1b), a compound first described by Plieninger,[4] is a stable indole-2,3-quinodimethane derivative which readily undergoes Diels–Alder reaction with alkynes to give, with concomitant loss of carbon dioxide, carbazoles.[1] We have now investigated the reaction of a series of pyranoindolones (1) with alkynes in more
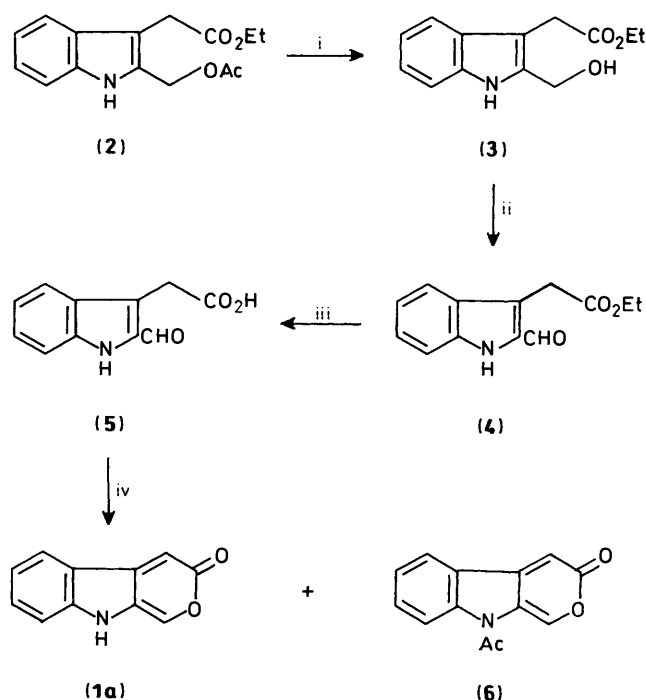

(1)

a, R = H; b, R = Me; c, R = Et; d, R = Pr;
e, R = Bu; f, R = C₅H₁₁; g, R = Prⁱ; h, R = Buᵗ

detail with the aims of (a) studying the steric and electronic effects on the reaction, particularly with regard to the regio-selectivity of the cycloaddition to unsymmetrical alkynes, and (b) extending the range of carbazoles that are available by this route, bearing in mind that simple di- or tri-substituted carbazoles are often difficult to prepare.[5] We now report in detail the results of this investigation.

Results and Discussion

Although 1-substituted pyrano[3,4-b]indol-3-ones are known,[1,4] the parent ring system (1a) has not previously been reported. This was prepared from the known ethyl 2-acetoxy-methylindol-3-ylacetate (2)[6] by selective hydrolysis to the 2-hydroxymethyl derivative (3) (95%), followed by oxidation (83%), hydrolysis (72%), and cyclisation in acetic anhydride (40%) (Scheme 1). The cyclised product (1a) was accompanied by a small amount of a second compound tentatively assigned as the N-acetyl derivative (6).
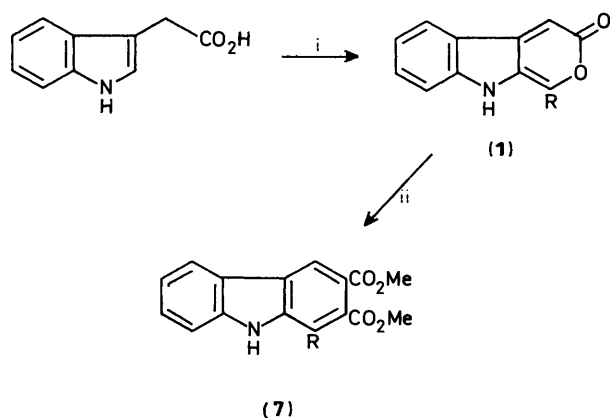
The pyranoindolones (1b)—(1h) were prepared by reaction of indol-3-ylacetic acid with the appropriate acid anhydride in the presence of boron trifluoride–diethyl ether exactly as described previously.[1,4] In the case of the butyl derivative (1e) the aqueous work-up caused partial hydrolysis to 2-pentanoylindol-3-yl-acetic acid, and in order to purify the pyranoindolone it was necessary to take the hydrolysis to completion by addition of aqueous methanolic sodium hydroxide followed by cyclo-

Scheme 1. Reagents: i, K₂CO₃, EtOH; ii, MnO₂, CH₂Cl₂; iii, NaOH, MeOH; iv, Ac₂O, reflux

dehydration in acetic anhydride. In this case the isolated yield of the pyranoindolone was lower (Table 1). The isopropyl and t-butyl derivatives (1g) and (1h) were also only isolated in low yield, because of difficulties in their purification.

The pyranoindolones (1) were all yellow-orange crystalline solids, although the parent compound (1a) appears to be less stable than the 1-substituted derivatives. As expected, the pyranoindolones (1) readily underwent Diels–Alder reaction with the reactive acetylene, dimethyl acetylenedicarboxylate (DMAD) on heating in bromobenzene or toluene–tetrahydro-furan (THF) to give, after aromatisation by loss of carbon dioxide, the carbazole 2,3-diesters (7) in good yield (Table 1). The 1-unsubstituted pyranoindolone (1a) is considerably more reactive than the 1-alkyl derivatives, and undergoes Diels–Alder reaction with DMAD at room temperature in THF over 20 h to

Table 1. Preparation of 1-alkylpyrano[3,4-*b*]indol-3-ones (1) and their reaction with dimethyl acetylenedicarboxylate
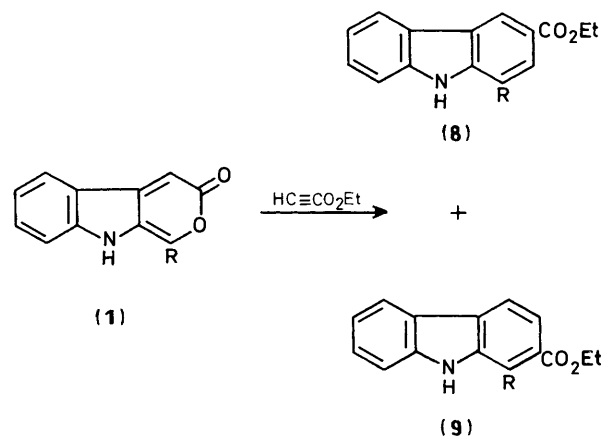

Reagents: i, (RCO)$_2$O, BF$_3$—Et$_2$O; ii, MeO$_2$CC≡CCO$_2$Me

(1), (7)	R	Yield (1) (%)	Yield (7) (%)
a	H	*a*	20—25
b	Me	66	81 [b]
c	Et	87	54
d	Pr	76	74
e	Bu	46 [c]	71
f	C$_5$H$_{11}$	62	88
g	Pr^i	24	89
h	Bu^t	15	—

[a] Prepared differently—see text. [b] Ref. 1. [c] Yield after purification by hydrolysis to the corresponding 2-acylindol-3-ylacetic acid and recyclisation.

Table 2. Reaction of 1-alkylpyrano[3,4-*b*]indol-3-ones (1) with ethyl propiolate

(1), (8), (9)	R	Combined yield (%)	Ratio
a	H	23	1.6:1
b	Me	74	1.7:1
c	Et	44	1.9:1
d	Pr	66	1.9:1
e	Bu	78	1.9:1
f	C$_5$H$_{11}$	77	2.5:1
g	Pr^i	62	4.0:1
h	Bu^t	50	>20:1 [a]

[a] Only a single product observed by 250 MHz ^{1}H n.m.r.

give the carbazole (7a) (25%), although the reaction is less clean than the corresponding reactions of the pyranoindolones (1b—h). In contrast, the 1-methylpyranoindolone (1b) shows little reaction with DMAD at room temperature, and only gave an 8% yield of the carbazole (7b) even after 137 h.
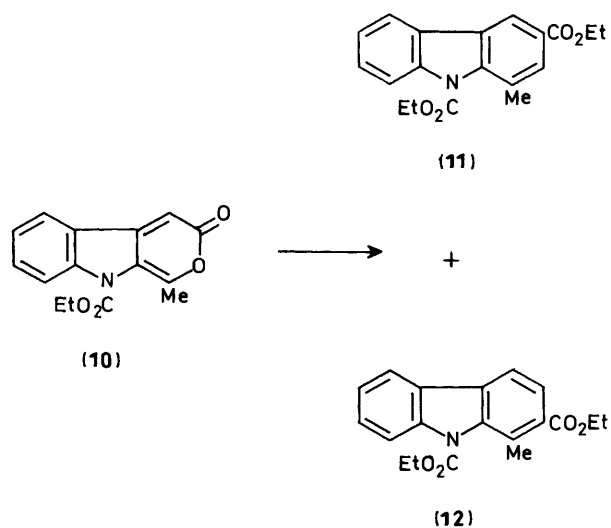
Since there was no dramatic substituent effect on the Diels–Alder reaction of the pyranoindolones (1) with DMAD, the reaction with the unsymmetrical alkyne, ethyl propiolate was investigated. Reaction of the parent pyranoindolone (1a) with ethyl propiolate in a refluxing mixture of toluene and THF (the THF is added to achieve complete dissolution) gave an inseparable mixture of the carbazoles (8a) and (9a) in the ratio of 1.6:1 as determined by integration of the 250 MHz ^{1}H n.m.r. spectrum of the mixture. Similarly, reaction of the pyrano-indolone (1b) with ethyl propiolate in boiling bromobenzene gave a chromatographically inseparable mixture of the carb-azoles (8b) and (9b) in the ratio 1.7:1, although in better yield. The structure of the major isomer, which could be separated by fractional crystallisation, was assigned as the 1,3-disubstituted carbazole (8b) by n.m.r. spectroscopy. Addition of Lewis acids (AlCl$_3$, Et$_3$Al, or TiCl$_4$) did not alter the ratio of products from this reaction, and simply resulted in lower yields and more complex reaction mixtures. The pyranoindolones (1c—g) also reacted with ethyl propiolate to give mixtures of the carbazoles (8c—g) and (9c—g), with the 1,3-disubstituted isomer (8) predominating over the 1,2-disubstituted carbazole (8) in every case (Table 2). The 1-t-butylpyranoindolone (1h), however, gave only the 1,3-disubstituted carbazole (8h) within the limits of 250 MHz ^{1}H n.m.r. detection.

The Diels–Alder reaction of the pyranoindolones (1) with ethyl propiolate therefore exhibits some degree of regio-
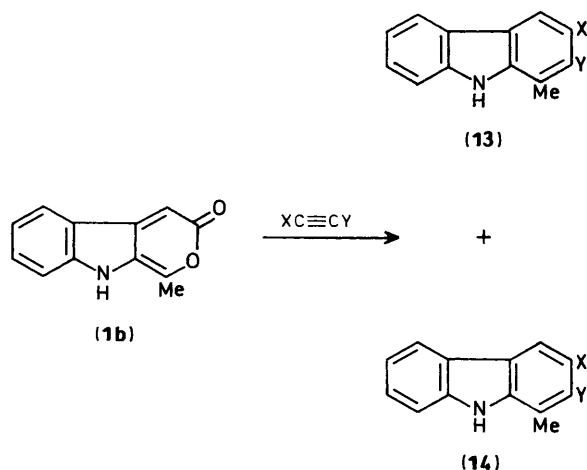

selectivity. The inherent preference for the formation of the carbazole 3-esters (8) suggests that the HOMO of the diene has a larger coefficient at C-1 than C-4, and hence in 'arrow pushing' terms the reaction is dominated by the nitrogen lone pair. Support for this comes from the reaction of the *N*-ethoxy-carbonylpyranoindolone (10), prepared by reaction of the pyranoindolone (1b) with ethyl cyanoformate (ethyl chloro-formate being unsatisfactory), with ethyl propiolate in which the regioselectivity of the Diels–Alder reaction was reversed. Thus heating the diene (10), bearing the electron-withdrawing

Table 3. Reaction of 1-methylpyrano[3,4-b]indol-3-one (**1b**) with unsymmetrical acetylenes

(13)

(1b)

XC≡CY ⟶ +

(14)

Entry	X	Y	(13), (14)	Combined yield (%)	Ratio
1	CO₂Me	H	a	84	1:1 [a]
2	COPr	H	b	87	2.8:1
3	Ph	H	c	32	>20:1 [b]
4	C₅H₁₁	H	d	16	>20:1 [b]
5	Buᵗ	H	e	8	>20:1 [b]
6	CO₂Me	Me	f	36	1:5
7	COPr	Me	g	42	1:3
8	CO₂Me	Ph	h	74	1:3.4
9	CO₂Me	Pr	i	33	1:10
10	CO₂Me	Buᵗ	j	28	1:>20 [b]
11	CO₂Me	PrCH(OH)	k	64	1:>20 [b,c]
12	CO₂Me	PrCO	l	93	1:1.2

[a] Ref. 1. [b] Only a single product observed by 250 MHz ¹H n.m.r. [c] Exists as the lactone (15)—see text.

group on nitrogen, with ethyl propiolate in refluxing bromo-benzene for 24 h (cf. 10 h for the corresponding NH compound) gave an 86% combined yield of the carbazoles (**11**) and (**12**) in the ratio 1 : 1.4. Hydrolysis of the mixture of (**11**) and (**12**) gave a mixture of (**8b**) and (**9b**) in the ratio 1 : 1.3 (cf. the ratio of 1.7 : 1 obtained in the reaction of the NH diene).
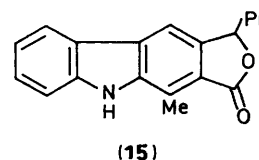
The regioselectivity of the Diels–Alder reaction of the 1-alkyl-pyranoindolones with ethyl propiolate also shows some dependence on the 1-alkyl substituent. The observed increases in regioselectivity are presumably steric in origin, with larger groups at the diene terminus reinforcing the inherent electronic preference for the formation of the 1,3-disubstituted carbazole (**8**).

In order to investigate the steric and electronic effect of substituents in the acetylenic dienophile, the 1-methyl pyrano-indolone (**1b**) was treated with a range of unsymmetrical alkynes (Table 3). The results fall into two groups. Just as with ethyl propiolate, terminal alkynes with the exception of methyl propiolate (entries 1—5) give mainly the 1,3-disubstituted carbazole (**13**), this isomer being the only product from the reactions with phenylacetylene, hept-1-yne, and t-butylacetylene. However, these last three alkynes react very slowly with the diene (**1b**), and the yields of carbazoles are poor compared with those obtained in the addition of methyl propiolate and hex-1-yn-3-one. Clearly an electron-withdrawing group on the alkyne facilitates the Diels–Alder reaction (cf. rapid reactions and good

yields obtained with DMAD, Table 1), and this further suggests that the reactions of the pyranoindolones (**1**) are 'normal' electron demand Diels–Alder additions, i.e. LUMO (dieno-phile)–HOMO (diene) controlled. Support for this comes from the failure of the pyranoindolone (**1b**) to react with the electron rich 1-ethoxyacetylene. Similarly, bis(trimethylsilyl)acetylene and diphenylacetylene did not react with the pyranoindolone (**1b**).

When the hydrogen atom of the terminal alkyne is replaced by a methyl group, an immediate difference in the Diels–Alder reaction with the pyranoindolone (**1b**) is observed. First, the reactions of the disubstituted alkynes are much slower and the yields of carbazole products lower (Table 3, Entries 1 and 2 vs. 6 and 7), and secondly the regioselectivity of the addition is reversed, in that the major products (**14f**) and (**14g**) have the electron withdrawing ester or ketone group in the 2-position. The marked difference in reactivity between terminal acetylenes and acetylenes where the terminal hydrogen is replaced by methyl has been noted before. For example, cyclopentadiene reacts readily with propiolic acid at room temperature to give the expected Diels–Alder adduct (43%)[7] whereas the corresponding reaction with but-2-ynoic acid requires a higher temperature and proceeds in lower yield.[8] Similarly propiolic acid reacts with cyclohexadiene at 70 °C, whereas but-2-ynoic acid fails to react at 100 °C,[8] and similar differences have been noted in the 1,3-dipolar cycloaddition reactions of methyl propiolate and methyl but-2-ynoate.[9] This difference in reactivity in cycloadditions is unlikely to be electronic in origin, and indeed theoretical calculations suggest that there is very little difference in the LUMO energies of propiolic acid (0.18 eV) and but-2-ynoic acid (0.08 eV),[10] so presumably the effects are steric in nature. Not surprisingly, the steric effect on the reaction is even more marked with the corresponding t-butyl-acetylene (Table 3, Entry 10).

The reactions of other substituted acetylenic esters (Table 3, entries 8—11) also give the carbazole 2-esters (**14h—k**) as the major products, the latter two reactions being totally regio-selective as evidenced by n.m.r. spectroscopy. In the case of the reaction with MeO₂CC≡CCH(OH)Pr, the initial carbazole product cyclises to the lactone (**15**) under the reaction

(15)

conditions.[11] The unsymmetrical acetylene containing two electron-withdrawing groups (Entry 12) reacts rapidly and in high yield with the pyranoindolone (**1b**) but is virtually unselective in its direction of addition, again indicating that an alkyl substituent on the triple bond is necessary for Diels–Alder reactions of the pyrone (**1b**) with alkynes to be highly regioselective.

Experimental

I.r. spectra were recorded as thin films or as solutions in chloroform on Perkin-Elmer 298 or 1710 spectrophotometers, and calibrated against polystyrene. ¹H N.m.r. were recorded on a Bruker WM250 (operating at 250 MHz), on a Perkin-Elmer R32 (operating at 90 MHz), or on a Varian EM360 spectrometer (operating at 60 MHz). Mass spectra were recorded on a V6 Micromass 707B mass spectrometer operating at 70 eV using a direct insertion probe. Silica gel (Merck type 60 H) was used for column chromatography. Ether refers to diethyl ether and light petroleum refers to the fraction b.p. 40—60 °C.

Tetrahydrofuran (THF) and ether were dried with potassium and sodium respectively, using the benzophenone ketyl radical as indicator. Other solvents were dried by standard procedures.

Preparation of Pyrano[3,4-b]indol-3-ones (1)

Pyrano[3,4-b]*indol-3-one* (**1a**).—Potassium carbonate (3.01 g, 21.82 mmol) was added in one portion to a stirred solution of ethyl 2-acetoxymethylindol-3-ylacetate[6] (**2**) (2.00 g, 7.27 mmol) in ethanol (50 ml). The mixture was stirred at room temperature for 30 min and then diluted with water (150 ml) and extracted with ether (2 × 80 ml). The combined ethereal extracts were washed with water (2 × 50 ml) and brine (50 ml), dried (MgSO$_4$), and concentrated under reduced pressure to give *ethyl 2-hydroxymethylindol-3-ylacetate* (**3**) (1.61 g, 95%), m.p. 112—113 °C (Found: C, 67.1; H, 6.5; N, 6.0. C$_{13}$H$_{15}$NO$_3$ requires C, 66.9; H, 6.5; N, 6.0%); ν$_{max.}$(Nujol) 3 472, 3 226, 1 714, 1 031, 1 008, 985, and 739 cm^{-1}; δ$_H$(90 MHz; CDCl$_3$) 1.23 (3 H, t, *J* 7 Hz), 3.35 (1 H, br, OH), 3.74 (2 H, s), 4.12 (2 H, q, *J* 7 Hz), 4.68 (2 H, s), 7.05—7.30 (3 H, m), 7.45—7.68 (1 H, m), and 8.82 (1 H, br, NH); *m/z* 233 (*M*$^+$, 69%), 216 (3), 204 (8), 187 (5), 160 (100), 158 (14), 146 (42), 142 (31), and 130 (28).

Manganese dioxide (6.02 g, 69.18 mmol) was added to a stirred solution of ethyl 2-hydroxymethylindol-3-ylacetate (**3**) (1.61 g, 6.91 mmol) in dry dichloromethane (70 ml), and the mixture was heated under reflux for 2 h. The hot reaction mixture was filtered through Celite, and the spent reagent washed well with dichloromethane. Concentration of the filtrate and chromatography of the residue (ether–light petroleum) gave *ethyl 2-formylindol-3-ylacetate* (**4**) (1.33 g, 83%), m.p. 79—80 °C (Found: C, 67.55; H, 5.7; N, 6.1. C$_{13}$H$_{13}$NO$_3$ requires C, 67.5; H, 5.7; N, 6.1%); ν$_{max.}$(Nujol) 3 309, 1 732, 1 656, 1 230, 1 167, 1 153, and 747 cm^{-1}; δ$_H$(250 MHz; CDCl$_3$) 1.23 (3 H, t, *J* 7 Hz), 4.08 (2 H, s), 4.16 (2 H, q, *J* 7 Hz), 7.14—7.20 (1 H, m), 7.32—7.43 (2 H, m), 7.75 (1 H, d, *J* 8 Hz), 9.27 (1 H, br, NH), and 10.05 (1 H, s, CHO); *m/z* 231 (*M*$^+$, 47%), 202 (3), 189 (9), 185 (20), 158 (100), and 130 (33).

Sodium hydroxide solution (1M; 20 ml) was added to a stirred solution of ethyl 2-formylindol-3-ylacetic acid (**4**) (1.33 g, 5.76 mmol) in methanol (50 ml). The mixture was stirred at room temperature until t.l.c. indicated completion of reaction, when it was diluted with water (50 ml) and extracted with ether (2 × 50 ml). The aqueous phase was acidified with dilute phosphoric acid and extracted with ether (3 × 70 ml). The combined ethereal extracts were washed with water (100 ml) and brine (100 ml), dried (MgSO$_4$), and concentrated to give a brown solid. Trituration with methanol gave 2-*formylindol-3-ylacetic acid* (**5**) (686 mg) as a pale yellow solid. The combined mother liquors were concentrated and chromatographed to give a further batch of the acid (**5**) (145 mg, total 831 mg, 72%), m.p. 197—200 °C (Found: C, 64.9; H, 4.5; N, 6.8. C$_{11}$H$_9$NO$_3$ requires C, 65.0; H, 4.5; N, 6.9%); ν$_{max.}$ 3 319, 1 704, 1 656, 1 225, 879, and 750 cm^{-1}; δ$_H$[250 MHz; (CD$_3$)$_2$CO] 4.20 (2 H, s), 7.14 (1 H, ~t, *J* 8 Hz), 7.36 (1 H, ~t, *J* 8 Hz), 7.52 (1 H, d, *J* 8 Hz), 7.80 (1 H, d, *J* 8 Hz), 10.15 (1 H, s), and 10.88 (1 H, br, NH) (CO$_2$H not observed); *m/z* 203 (*M*$^+$, 52%), 185 (14), 159 (93), 158 (100), and 130 (85).

A solution of 3-formylindol-3-ylacetic acid (**5**) (245 mg, 1.21 mmol) in acetic anhydride (25 ml) was heated under reflux for 1.5 h. The acetic anhydride was evaporated under reduced pressure and the residue chromatographed (ether–methanol) to give (*i*) the *title compound* (**1a**) (90 mg, 40%), m.p. darkens *ca.* 165 °C (Found: *M*$^+$, 185.0482. C$_{11}$H$_7$NO$_2$ requires *M*, 185.0477); ν$_{max.}$(CHCl$_3$) 3 465, 1 695, 1 659, 1 617, 1 569, and 1 111 cm^{-1}; δ$_H$[250 MHz; (CD$_3$)$_2$CO] 6.64 (1 H, d, *J* 2 Hz), 7.05 (1 H, ~t, *J* 8 Hz), 7.24 (1 H, d, *J* 8 Hz), 7.50 (1 H, ~t, *J* 8 Hz), 7.92 (1 H, d, *J* 2 Hz), 7.98 (1 H, d, *J* 8 Hz), and 9.34 (1 H, br, NH); *m/z* 185 (*M*$^+$, 100%), 157 (29), and 129 (44), and (*ii*) 9-acetylpyrano[3,4-

b]indol-3-one (**6**) (10 mg, 4%), m.p. 210—215 °C, ν$_{max.}$(CHCl$_3$) 1 759, 1 703, 1 657, 1 573, 1 467, 1 374, and 1 309; δ$_H$[250 MHz; (CD$_3$)$_2$CO] 2.78 (3 H, s), 6.70 (1 H, d, *J* 1.5 Hz), 7.42 (1 H, ~t, *J* 8 Hz), 7.73 (1 H, ~t, *J* 8 Hz), 7.97 (1 H, br d, *J* 8 Hz), 8.15 (1 H, d, *J* 8 Hz), and 8.69 (1 H, br s); *m/z* 227 (*M*$^+$, 32%), 185 (100), 157 (34), and 129 (48).

1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**).—Prepared as previously described.[1]

1-*Ethylpyrano*[3,4-b]*indol-3-one* (**1c**).—Freshly distilled boron trifluoride–diethyl ether (1 ml) was added dropwise over 1 h to a stirred solution of indol-3-ylacetic acid (1.05 g, 6 mmol) in propionic anhydride (3 ml) at 0 °C. The mixture was allowed to warm to room temperature and stirred for a further 0.5 h. Ether (30 ml) was added and the orange solid was filtered off, washed with ether (25 ml), triturated with aqueous sodium hydrogen carbonate (half saturated; 3 × 25 ml), washed with water (3 × 25 ml), and dried *in vacuo* to give the title compound (**1c**) (1.11 g, 87%), m.p. 188—190 °C (lit.,[4] m.p. 189—191 °C); ν$_{max.}$(Nujol) 3 380br, 1 660, 1 557, 1 533, 960, and 905 cm^{-1}; δ$_H$[250 MHz; (CD$_3$)$_2$SO] 1.24 (3 H, t, *J* 7.5 Hz), 2.38 (2 H, q, *J* 7.5 Hz), 6.55 (1 H, s, C=CHCO–O), 7.0 (1 H, ~t, *J* 7.8 Hz), 7.20 (1 H, d, *J* 8.2 Hz), 7.50 (1 H, ~t, *J* 8.2 Hz), 7.97 (1 H, d, *J* 7.8 Hz), and 10.47 (1 H, br); *m/z* 213 (*M*$^+$, 100%), 198 (5), 185 (29), 184 (15), 170 (76), and 156 (27).

1-*Propylpyrano*[3,4-b]*indol-3-one* (**1d**).—Addition of freshly distilled boron trifluoride–diethyl ether (2 ml) to a stirred solution of indol-3-ylacetic acid (2.1 g, 12 mmol) in butyric anhydride (7 ml) at 0 °C as described above, followed by a similar work-up gave the title compound (**1d**) (2.08 g, 76%), m.p. 187—190 °C (EtOAc) (lit.,[4] m.p. 187—190 °C); ν$_{max.}$(Nujol) 3 160br, 1 694, 1 630, 1 615, 1 565, 1 320, 740, and 728 cm^{-1}; δ$_H$[250 MHz; (CD$_3$)$_2$SO] 0.93 (3 H, t, *J* 7.4 Hz), 1.61—1.79 (2 H, m), 2.78 (2 H, t, *J* 7.4 Hz), 6.55 (1 H, s, C=CHCO$_2$) 6.99 (1 H, ~t, *J* 7.8 Hz), 7.20 (1 H, d, *J* 8.2 Hz), 7.49 (1 H, ~t, *J* 8.2 Hz), 7.97 (1 H, d, *J* 8.2 Hz), and 10.47 (1 H, br); *m/z* 227 (*M*$^+$, 100%), 198 (41), 170 (74), and 156 (23).

1-*Butylpyrano*[3,4-b]*indol-3-one* (**1e**).—Freshly distilled boron trifluoride–diethyl ether (2 ml) was added dropwise over 1 h to a stirred solution of indol-3-ylacetic acid (1.98 g, 11.3 mmol) in valeric anhydride (8 ml) at 0 °C. The mixture was allowed to warm to room temperature and stirred for a further 0.5 h. Ether (50 ml) was added and the orange solid was filtered off, washed with more ether (50 ml), triturated with aqueous sodium hydrogen carbonate (half saturated; 3 × 50 ml), and washed with water (3 × 50 ml). The solid was then taken up in aqueous sodium hydroxide (1M; 25 ml) and methanol (10 ml) and the mixture heated on a steam-bath for 1 h. After cooling to 0 °C the reaction mixture was acidified with concentrated hydrochloric acid and diluted with water (50 ml). The resulting white solid was filtered off, washed with water (50 ml), and dried *in vacuo* overnight. The dry solid was taken up in acetic anhydride (30 ml) and the mixture heated at reflux under nitrogen for 3 h. After cooling to room temperature, the mixture was diluted with water (100 ml) and thoroughly shaken. The resulting orange solid was filtered off, washed with ether (20 ml), dilute aqueous sodium hydrogen carbonate (50 ml), and water (50 ml), and dried *in vacuo* to give the *title compound* (**1e**) (1.26 g, 46%), m.p. 160—163 °C (Found: C, 74.5; H, 6.3; N, 5.8. C$_{15}$H$_{15}$NO$_2$ requires C, 74.7; H, 6.3; N, 5.8%); ν$_{max.}$(Nujol) 3 150br, 1 693, 1 628, 1 610, 1 560, 1 320, 1 228, and 724 cm^{-1}; δ$_H$[250 MHz; (CD$_3$)$_2$SO] 0.90 (3 H, t, *J* 7.3 Hz), 1.27—1.42 (2 H, m, CH$_2$), 1.60—1.72 (2 H, m, CH$_2$), 2.81 (2 H, t, *J* 7.3 Hz), 6.53 (1 H, s, C=CHCOO), 6.99 (1 H, ~t, *J* 7.9 Hz), 7.20 (1 H, d, *J* 8.2 Hz), 7.49 (1 H, ~t, *J* 8.2 Hz), 7.95 (1 H, d, *J* 7.9 Hz), and

10.46 (1 H, br, NH); m/z 241 (M^+, 100%), 213 (7), 198 (35), and 170 (61).

1-Pentylpyrano[3,4-b]*indol-3-one* (**1f**).—Addition of freshly distilled boron trifluoride–diethyl ether (3 ml) to a stirred solution of indol-3-ylacetic acid (3.11 g, 17.8 mmol) in hexanoic anhydride (10 ml) at 0 °C as described for compound (**1c**), followed by a similar work-up gave the *title compound* (**1f**) (2.80 g, 62%), m.p. 178—181 °C (EtOAc) (Found: C, 75.2; H, 6.75; N, 5.45. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $v_{max.}$(Nujol) 3 140 br, 1 690, 1 622, 1 610, 1 558, 1 320, 1 225, 1 150, and 818 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 0.84 (3 H, t, J 6.6 Hz), 1.20—1.39 (4 H, m), 1.6—1.75 (2 H, m), 2.79 (2 H, t, J 7.4 Hz), 6.54 (1 H, s, C=CHCOO), 6.99 (1 H, ~t, J 7.8 Hz), 7.20 (1 H, d, J 8.2 Hz), 7.49 (1 H, ~t, J 8.2 Hz), 7.96 (1 H, d, 7.8 Hz), and 10.46 (1 H, br); m/z 255 (M^+, 100%), 227 (6), 198 (38), 184 (24), and 170 (52).

1-Isopropylpyrano[3,4-b]*indol-3-one* (**1g**).—Addition of freshly distilled boron trifluoride–diethyl ether (1 ml) to a stirred solution of indol-3-ylacetic acid (1.0 g, 5.71 mmol) in isobutyric anhydride (4.5 ml) at 0 °C as described above, followed by similar work-up and chromatography gave the *title compound* (**1g**) as a bright yellow solid (317 mg, 24%), m.p. 180—184 °C (Found: C, 74.2; H, 5.9; N, 6.0. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%); $v_{max.}$(Nujol) 3 200br, 1 696, 1 630, 1 575, 1 321, 1 220, 1 120, 750, and 650 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 1.27 (6 H, d, J 6.9 Hz), 3.29 (1 H, hept, J 6.9 Hz), 6.55 (1 H, s), 7.00 (1 H, ~t, J 8 Hz), 7.20 (1 H, d, J 8 Hz), 7.50 (1 H, ~t, J 8 Hz), 7.96 (1 H, d, J 8 Hz), and 10.42 (1 H, br, NH); m/z 227 (M^+, 100%), 212 (24), 199 (8), 184 (81), 170 (6), 156 (38), and 128 (37).

1-t-Butylpyrano[3,4-b]*indol-3-one* (**1h**).—Addition of freshly distilled boron trifluoride–diethyl ether (1 ml) to a stirred solution of indol-3-ylacetic acid (1.0 g, 5.71 mmol) in tri-methylacetic anhydride (5 ml) at 0 °C as described above, followed by similar work-up and chromatography gave the *title compound* (**1h**) as a bright yellow solid (212 mg, 15%), m.p. 164—168 °C (Found: M^+, 241.1096. $C_{15}H_{15}NO_2$ requires M, 241.1103); $v_{max.}$(Nujol) 3 300br, 1 680, 1 615, 1 558, and 750 cm^{-1}; δ_H[250 MHz; $(CD_3)_2CO$] 1.48 (9 H, s), 6.50 (1 H, s, C=CHCOO), 7.03 (1 H, ~t, J 8 Hz), 7.24 (1 H, d, J 8.2 Hz), 7.49 (1 H, ~t, J 8.2 Hz), 7.96 (1 H, d, J 8 Hz), and 9.12 (1 H, br, NH); m/z 241 (M^+, 100%), 226 (37), 198 (37), 184 (91), 156 (38), 128 (38), and 57 (51).

Ethyl 1-Methyl-3-oxopyrano[3,4-b]*indole-9-carboxylate* (**10**).—A solution of the pyranoindolone (**1b**) (152 mg, 0.76 mmol) and ethyl cyanoformate (378 mg, 3.82 mmol) in bromobenzene (8 ml) was heated under reflux for 14 h. The mixture was then evaporated and the residue chromatographed to give the *title compound* (**10**) (134 mg, 65%), m.p. 144—146 °C (Found: C, 66.4; H, 4.7; N, 5.15. $C_{15}H_{13}NO_4$ requires C, 66.4; H, 4.8; N, 5.2%); $v_{max.}$(Nujol) 1 745, 1 710, and 1 608 cm^{-1}; δ_H[250 MHz; CDCl$_3$] 1.45 (3 H, t, J 6.8 Hz), 2.53 (3 H, s), 4.44 (2 H, q, J 6.8 Hz), 6.42 (1 H, s), 7.30 (1 H, ddd, J 7.6, 7.6, and 1.0 Hz), 7.58 (1 H, ddd, J 7.6, 7.6, and 1.4 Hz), 7.77 (1 H, d, J 7.6 Hz), and 7.99 (1 H, d, J 7.6 Hz); m/z 271 (M^+, 93%) and 198 (100).

Reaction of the Pyranoindolones (1) with DMAD

Reaction of Pyrano[3,4-b]*indol-3-one* (**1a**) *with DMAD*.—A mixture of the pyranoindole (**1a**) (26 mg, 0.14 mmol) and DMAD (67 mg, 0.47 mmol) in THF (5 ml) was stirred at room temperature for 20 h. The mixture was then evaporated and the residue chromatographed to give dimethyl 9H-carbazole-2,3-dicarboxylate (**7a**) (10 mg, 25%), m.p. 130—131 °C (lit.,[12] 136—137 °C); $v_{max.}$(CHCl$_3$) 3 466, 1 719, 1 436, 1 348, 1 266, 1 111, and 1 070 cm^{-1}; δ_H[250 MHz; $(CD_3)_2CO$] 3.86 (3 H, s), 3.87

(3 H, s), 7.29 (1 H, ~t, J 8 Hz), 7.50 (1 H, ~t, J 8 Hz), 7.62 (1 H, d, J 8 Hz), 7.80 (1 H, s), 8.28 (1 H, d, J 8 Hz), 8.60 (1 H, s), and 10.92 (1 H, br, NH); m/z 283 (M^+, 82%) and 252 (100).

In a refluxing mixture of THF–toluene the above reaction was complete within 2 h, and carbazole (**7a**) was obtained in 20% yield.

Reaction of 1-Methylpyrano[3,4-b]*indol-3-one* (**1b**) *with DMAD*.—This reaction has been reported previously,[1] and gave the carbazole (**7b**) (81%).

Reaction of 1-Ethylpyrano[3,4-b]*indol-3-one* (**1c**) *with DMAD*.—A mixture of the pyranoindole (**1c**) (181 mg, 0.85 mmol) and DMAD (241 mg, 1.7 mmol) in bromobenzene (45 ml) was refluxed under nitrogen for 3 h. The mixture was evaporated and the residue chromatographed (dichloro-methane–light petroleum) to give dimethyl 1-ethyl-9H-carb-azole-2,3-dicarboxylate (**7c**) (143 mg, 54%) m.p. 163—164 °C, (lit.,[4] m.p. 157—158 °C) (Found: C, 69.4; H, 5.4; N, 4.5. Calc. for $C_{18}H_{17}NO_4$: C, 69.4; H, 5.5; N, 4.5%); $v_{max.}$(Nujol) 3 265br, 1 720, 1 695, 1 241, and 740 cm^{-1}; δ_H[250 MHz; CDCl$_3$] 1.33 (3 H, t, J 7.6 Hz), 2.88 (2 H, q, J 7.6 Hz), 3.94 (3 H, s), 4.00 (3 H, s), 7.26—7.33 (1 H, m), 7.43—7.51 (2 H, m), 8.09 (1 H, d, J 7.8 Hz), 8.50 (1 H, br), and 8.63 (1 H, s); m/z 311 (M^+, 89%), 280 (78), 279 (100), 264 (63), 221 (82), and 193 (47).

Reaction of 1-Propylpyrano[3,4-b]*indol-3-one* (**1d**) *with DMAD*.—A mixture of the pyranoindole (**1f**) (116 mg, 0.45 mmol) and DMAD (704 mg, 4.98 mmol) in toluene–THF (9:1, 80 ml) was refluxed under nitrogen for 36 h. The mixture was evaporated and the residue chromatographed to give dimethyl 1-propyl-9H-carbazole-2,3-dicarboxylate (**7d**) (595 mg, 74%), m.p. 100—101 °C (Found: C, 69.9; H, 5.8; N, 4.4. $C_{19}H_{19}NO_4$ requires C, 70.1; H, 5.9; N, 4.3%); $v_{max.}$(Nujol) 3 355, 1 725, 1 689, 1 355, 1 250, and 680 cm^{-1}; δ_H (250 MHz; CDCl$_3$) 1.05 (3 H, t, J 7.3 Hz), 1.69—1.82 (2 H, m), 2.85 (2 H, ~t, J 8 Hz), 3.95 (3 H, s), 4.00 (3 H, s), 7.26—7.35 (1 H, m), 7.45—7.53 (2 H, m), 8.10 (1 H, d, J 7.8 Hz), 8.35 (1 H, br), and 8.65 (1 H, s); m/z 325 (M^+, 89%), 294 (56), 293 (79), 278 (90), 261 (26), 250 (11), and 28 (100).

Reaction of 1-Butylpyrano[3,4-b]*indol-3-one* (**1e**) *with DMAD*.—A mixture of the pyranoindole (**1e**) (273 mg, 1.13 mmol) and DMAD (322 mg, 2.27 mmol) in bromobenzene (50 ml) was heated under reflux for 4 h. The mixture was evaporated and the residue chromatographed to give dimethyl 1-butyl-9H-carbazole-2,3-dicarboxylate (**7e**) (232 mg, 71%), m.p. 133.5—134.5 °C (Found: C, 70.55; H, 6.1; N, 4.1. $C_{20}H_{21}NO_4$ requires C, 70.8; H, 6.2; N, 4.1%); $v_{max.}$(Nujol) 3 340br, 1 720, 1 708, 1 255, and 750 cm^{-1}; δ_H[250 MHz; CDCl$_3$] 0.93 (3 H, t, J 7.3 Hz), 1.36—1.50 (2 H, m), 1.64—1.74 (2 H, m), 2.84 (2 H, ~t, J 8 Hz), 3.91 (3 H, s), 3.98 (3 H, s), 7.24—7.31 (1 H, m), 7.41—7.50 (2 H, m), 8.07 (1 H, d, J 7.8 Hz), 8.40 (1 H, br), and 8.60 (1 H, s); m/z 339 (M^+, 61%), 308 (35), 307 (36), 278 (100), and 250 (10).

Reaction of 1-Pentylpyrano[3,4-b]*indol-3-one* (**1f**) *with DMAD*.—A mixture of the pyranoindole (**1f**) (116 mg, 0.45 mmol) and DMAD (129 mg, 0.91 mmol) in toluene (30 ml) was refluxed under nitrogen for 36 h. The mixture was evaporated and the residue chromatographed to give dimethyl 1-pentyl-9H-carbazole-2,3-dicarboxylate (**7f**) (142 mg, 88%), m.p. 142—143 °C (Found: C, 71.5; H, 6.55; N, 3.8. $C_{21}H_{23}NO_4$ requires C, 71.4; H, 6.6; N, 4.0%); $v_{max.}$(Nujol) 3 378br, 1 730, 1 693, 1 254, 750, and 740 cm^{-1}; δ_H (250 MHz; CDCl$_3$) 0.88 (3 H, t, J 6.9 Hz), 1.24—1.48 (4 H, m), 1.64—1.79 (2 H, m), 2.84 (2 H, ~t, J 8 Hz), 3.93 (3 H, s), 4.00 (3 H, s), 7.26—7.32 (1 H, m), 7.43—7.51 (2 H, m), 8.07 (1 H, d, J 7.8 Hz), 8.47 (1 H, br), and 8.61 (1 H, s); m/z 353 (M^+, 60%), 322 (35), 321 (45), 296 (17), and 278 (100).

Reaction of 1-*Isopropylpyrano*[3,4-b]*indol*-3-*one* (**1g**) *with DMAD*.—A mixture of the pyranoindole (**1g**) (22 mg, 0.097 mmol) and DMAD (28 mg, 0.2 mmol) in bromobenzene (4 ml) was refluxed under nitrogen for 12 h. The mixture was evaporated and the residue chromatographed to give *dimethyl* 1-*isopropyl*-9*H*-*carbazole*-2,3-*dicarboxylate* (**7g**) (28 mg, 89%), m.p. 205—207 °C (Found: C, 70.1; H, 5.9; N, 4.4. $C_{19}H_{19}NO_4$ requires C, 70.1; H, 5.9; N, 4.3%); $v_{max.}$(Nujol) 3 398, 1 711, 1 707sh, 1 600, 1 242, and 740 cm⁻¹; δ_H(250 MHz; CDCl₃) 1.51 (6 H, d, *J* 7.1 Hz), 3.23—3.34 (1 H, hept, *J* 7.1 Hz), 3.92 (3 H, s), 3.99 (3 H, s), 7.24—7.31 (1 H, m), 7.43—7.52 (2 H, m), 8.10 (1 H, d, *J* 7.8 Hz), 8.45 (1 H, br), and 8.67 (1 H, s); *m*/*z* 325 (*M*⁺, 59%), 294 (41), 293 (54), 278 (58), and 235 (100).

Reaction of the Pyranoindolones (1) with Ethyl Propiolate

Reaction of Pyrano[3,4-b]*indol*-3-*one* (**1a**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1a**) (41 mg, 0.22 mmol) and ethyl propiolate (206 mg, 2.1 mmol) in THF (6 ml) and toluene (6 ml) was heated under reflux for 10 h. The mixture was evaporated and the residue chromatographed to give ethyl 9*H*-carbazole-3-carboxylate (**8a**) and ethyl 9*H*-carbazole-2-carboxylate (**9a**) (1.6:1) (12.2 mg, 23%), $v_{max.}$(CHCl₃) 3 470, 1 703, 1 328, 1 303, 1 253, and 1 097 cm⁻¹; δ_H[250 MHz; (CD₃)₂CO] 1.36—1.43 (m, ethoxy CH₃, both isomers), 4.37 (q, *J* 7 Hz, OCH₂, both isomers), 7.20—7.29 (m, both isomers), 7.41—7.50 (m, both isomers), 7.54—7.60 (m, both isomers), 7.87 (1 H, dd, *J* 8 and 1.5 Hz, minor), 8.08 (1 H, dd, *J* 8, and 1.5 Hz, major, 2-H), 8.17—8.26 (m, both isomers), 8.83 (1 H, d, *J* 1.5 Hz, major, 4-H), 10.63 (1 H, br, major, NH), and 10.76 (1 H, br, minor, NH); *m*/*z* 239 (*M*⁺, 100%), 194 (71), and 166 (28).

Reaction of 1-*Methylpyrano*[3,4-b]*indol*-3-*one* (**1b**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1b**) (257 mg, 1.29 mmol) and ethyl propiolate (379 mg, 3.87 mmol) in bromobenzene (50 ml) was heated at reflux under nitrogen for 10 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-methyl-9*H*-carbazole-3-carboxylate (**8b**) and ethyl 1-methyl-9*H*-carbazole-2-carboxylate (**9b**) (1.7:1) (242 mg, 74%). The isomers were characterised as a mixture (Found: C, 75.7; H, 6.0; N, 5.5. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); $v_{max.}$(Nujol) 3 395, 3 340, 1 680, 1 628, 1 605, 1 260, 770, 760, 750, and 734 cm⁻¹; δ_H[250 MHz; (CD₃)₂CO] 1.36—1.42 (2 × t, ethoxy CH₃, *J* 7.5 Hz, both isomers), 2.61 (3 H, s, CH₃, major), 2.83 (3 H, s, CH₃, minor), 4.31—4.41 (2 × q, *J* 6.8 Hz, OCH₂, both isomers), 7.17—7.27 (m, both isomers), 7.40—7.47 (m), 7.54—7.58 (m), 7.75 (1 H, d, *J* 8 Hz, minor), 7.90 (1 H, s, major, 2-H), 8.00 (1 H, d, *J* 8 Hz, minor), 8.13 (1 H, d, *J* 7.6 Hz, minor, 5-H), 8.20 (1 H, d, *J* 7.6 Hz, major, 5-H), 8.67 (1 H, s, major, 4-H), 10.59 (1 H, br, minor, NH), and 10.71 (1 H, br, major, NH); *m*/*z* 253 (*M*⁺, 100%), 238 (3), 224 (15), 208 (57), and 180 (33).

It was possible to separate the major isomer by fractional crystallisation from dichloromethane–hexane; *ethyl* 1-*methyl*-9H-*carbazole*-3-*carboxylate* (**8b**), m.p. 151—153 °C, $v_{max.}$(Nujol) 3 340, 1 682, 1 605, 1 260, 770, and 734 cm⁻¹; δ_H(250 MHz; CDCl₃) 1.44 (3 H, t, *J* 7.5 Hz), 2.57 (3 H, s), 4.41 (2 H, q, *J* 6.8 Hz), 7.25 (1 H, ~t, *J* 7.4 Hz), 7.39—7.48 (2 H, m), 7.95 (1 H, s), 8.1 (1 H, d, *J* 7.6 Hz), 8.26 (1 H, br), and 8.66 (1 H, s).

Reaction of 1-*Ethylpyrano*[3,4-b]*indol*-3-*one* (**1c**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1c**) (216 mg, 1.01 mmol) and ethyl propiolate (444 mg, 4.53 mmol) in bromobenzene (55 ml) was refluxed under nitrogen for 5 h. The solvent was evaporated and the residue chromatographed to give ethyl 1-ethyl-9*H*-carbazole-2-carboxylate (**9c**) and ethyl 1-ethyl-9*H*-carbazole-3-carboxylate (**8c**) (1:1.86; 120 mg, 44%). The isomer ratio was determined by the benzylic proton integrals in the ¹H

n.m.r. spectrum. The isomers were not separable by column chromatography and were thus characterised as a mixture (Found: C, 76.5; H, 6.4; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.2%); $v_{max.}$(Nujol) 3 340, 1 678, 1 340, 1 260, 770, and 738 cm⁻¹; δ_H(250 MHz; CDCl₃) 1.36—1.49 (m, 4 × CH₃, both isomers), 2.94 (2 H, q, *J* 7.6 Hz, benzylic CH₂, major), 3.28 (2 H, 1, *J* 7.6 Hz, benzylic CH₂, minor), 4.37—4.49 (2 × q, OCH₂, both isomers), 7.14—7.35 (m, both isomers), 7.41—7.51 (m, both isomers), 7.81 (1 H, d, *J* 8.2 Hz, minor), 7.93 (1 H, d, *J* 8.2 Hz, minor), 7.99 (1 H, s, major, 2-H), 8.07—8.13 (m, both isomers), 8.30—8.33 (br, NH, both isomers), and 8.69 (1 H, s, major, 4-H); *m*/*z* 267 (*M*⁺, 100%), 252 (17), 239 (8), 222 (47), and 194 (20).

Reaction of 1-*Propylpyrano*[3,4-b]*indol*-3-*one* (**1d**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1d**) (296 mg, 1.30 mmol) and ethyl propiolate (255 mg, 2.6 mmol) in bromobenzene (25 ml) was refluxed under nitrogen for 6 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-propyl-9*H*-carbazole-2-carboxylate (**9d**) and ethyl 1-propyl-9*H*-carbazole-3-carboxylate (**9d**) and ethyl 1-propyl-9*H*-carbazole-3-carboxylate (**8d**) (1:1.9; 224 mg, 66%). The isomers were characterised as a mixture (Found: C, 76.7; H, 6.8; N, 5.0. $C_{18}H_{19}NO_2$ requires C, 76.8; H, 6.8; N, 5.0%); $v_{max.}$(Nujol) 3 415, 3 358, 1 690, 1 678, 1 240, 1 138, and 750 cm⁻¹; δ_H[250 MHz; (CD₃)₂CO] 0.98—1.08 (m, propyl CH₃, both isomers), 1.39 (2 × t, *J* 7.0 Hz, ethoxy CH₃, both isomers), 1.72—1.9 (m, propyl CH₂, both isomers), 2.98 (2 H, t, *J* 8 Hz, major), 3.30 (2 H, ~t, *J* 8 Hz, minor), 4.31—4.42 (2 × q, OCH₂, both isomers), 7.16—7.27 (m, both isomers), 7.39—7.47 (m), 7.5—7.58 (m), 7.73 (1 H, d, *J* 8.0 Hz, minor), 7.92 (1 H, s, major), 8.01 (1 H, d, *J* 8 Hz, minor), 8.15 (1 H, d, *J* 8 Hz, minor, 5-H), 8.21 (1 H, d, *J* 8 Hz, major, 5-H), 8.69 (1 H, s, major, 4-H), 10.68 (1 H, br, minor), and 10.79 (1 H, br, major); *m*/*z* 281 (*M*⁺, 100%), 252 (63), 236 (25), 224 (25), and 208 (5).

Reaction of 1-*Butylpyrano*[3,4-b]*indol*-3-*one* (**1e**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1a**) (157 mg, 0.65 mmol) and ethyl propiolate (128 mg, 1.31 mmol) in bromobenzene (25 ml) was heated under reflux for 6 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-butyl-9*H*-carbazole-2-carboxylate (**9e**) and ethyl 1-butyl-9*H*-carbazole-3-carboxylate (**8e**) (1:1.88; 150 mg, 78%). The isomer ratio was determined by the benzylic proton integrals in the ¹H n.m.r. spectrum. The isomers were not separable by column chromatography and were thus characterised as a mixture (Found: C, 77.0; H, 7.0; N, 4.8. $C_{19}H_{21}NO_2$ requires C, 77.3; H, 7.2; N, 4.7%); $v_{max.}$(Nujol) 3 375, 1 698sh 1 689, 1 370, 1 240, 1 225, and 740 cm⁻¹; δ_H[250 MHz; (CD₃)₂CO] 0.91—0.97 (2 × t, butyl CH₃, both isomers), 1.36—1.55 (m, butyl CH₂ and ethoxy CH₃, both isomers), 1.65—1.83 (m, butyl CH₂, both isomers), 3.01 (2 H, t, *J* 7.7 Hz, benzylic CH₂, major), 3.33 (2 H, t, *J* 8 Hz, benzylic CH₂, minor), 4.32—4.41 (2 × q, OCH₂, both isomers), 7.16—7.27 (m, both isomers), 7.39—7.45 (m, both isomers), 7.51—7.56 (m, both isomers), 7.73 (1 H, d, *J* 8.3 Hz, minor), 7.92 (1 H, s, major), 8.02 (1 H, d, *J* 8.3 Hz, minor), 8.14 (1 H, d, *J* 8.5 Hz, minor), 8.20 (1 H, d, *J* 8.5 Hz, major), 8.68 (1 H, s, major), 10.62 (1 H, br, minor), and 10.74 (1 H, br, major); *m*/*z* 295 (*M*⁺, 100%), 252 (16), 250 (22), 224 (76), and 180 (29).

Reaction of 1-*Pentylpyrano*[3,4-b]*indol*-3-*one* (**1f**) *with Ethyl Propiolate*.—A mixture of the pyranoindole (**1f**) (140 mg, 0.55 mmol) and ethyl propiolate (107 mg, 1.10 mmol) in toluene (30 ml) was refluxed under nitrogen for 48 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-pentyl-9*H*-carbazole-2-carboxylate (**9f**) and ethyl 1-pentyl-9*H*-carbazole-3-carboxylate (**8f**) (1:2.5; 131 mg, 77%). The isomer ratio was determined by the benzylic proton integrals in

the ^{1}H n.m.r. spectrum. The isomers were characterised as a mixture (Found: C, 77.5; H, 7.45; N, 4.5. $C_{20}H_{23}NO_2$ requires C, 77.6; H, 7.5; N, 4.5%); $v_{max.}$(Nujol) 3 365; 3 360, 1 691, 1 685, 1 240, 1 222, 1 025, 763, and 735 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 0.87—0.93 (m, pentyl CH$_3$, both isomers), 1.35—1.51 (m, pentyl CH$_2$ and ethoxy CH$_3$, both isomers), 1.70—1.85 (m, pentyl CH$_2$, both isomers), 2.89 (2 H, t, J 7.8 Hz, benzylic CH$_2$, major), 3.25 (2 H, t, J 7.8 Hz, benzylic CH$_2$, minor), 4.36—4.49 (2 × q, J 7.1 Hz, OCH$_2$, both isomers), 7.20—7.31 (m, both isomers), 7.41—7.51 (m, both isomers), 7.81 (1 H, d, J 8.2 Hz, minor), 7.93 (1 H, d, J 8.2 Hz, minor), 7.96 (1 H, s, major), 8.07—8.30 (m, both isomers), 8.26 (1 H, br, NH, minor), 8.33 (1 H, br, NH, major), and 8.67 (1 H, s, major, 4-H); m/z 309 (M^+, 100%), 264 (14), 252 (50), and 224 (26).

Reaction of 1-Isopropylpyrano[3,4-b]indol-3-one (**1g**) *with Ethyl Propiolate.*—A mixture of the pyranoindole (**1g**) (102 mg, 0.45 mmol) and ethyl propiolate (132 mg, 1.34 mmol) in bromobenzene (10 ml) was heated under reflux for 16 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-isopropyl-9H-carbazole-2-carboxylate (**9g**) and ethyl 1-isopropyl-9H-carbazole-3-carboxylate (**8g**) (1:4; 78 mg, 62%). The isomers were characterised as a mixture (Found: C, 76.7, H, 6.8; N, 5.0. $C_{18}H_{19}NO_2$ requires C, 76.8; H, 6.8; N, 5.0%); $v_{max.}$(Nujol) 3 350, 3 290, 1 680, 1 600, 1 250, and 740 cm^{-1}; δ_H[250 MHz; (CD$_3$)$_2$CO] 1.34—1.51 (m, ethoxy CH$_3$ of both isomers and isopropyl of major), 1.54 (6 H, d, J 6.9 Hz, isopropyl, minor), 3.47—3.58 (1 H, hept, J 6.9 Hz benzylic CH, major), 3.89—3.98 (1 H, hept, J 6.9 Hz benzylic CH, minor), 4.32—4.43 (m, OCH$_2$, both isomers), 7.16—7.28 (m, both isomers), 7.38—7.46 (m), 7.55—7.60 (m), 8.00 (1 H, s, major), 8.11 (1 H, d, J 7.9 Hz, minor), 5-H), 8.20 (1 H, d, J 7.9 Hz, major, 5-H), 8.69 (1 H, s, major), 10.35 (1 H, br, minor), and 10.73 (1 H, br, major); m/z 281 (M^+, 100%), 266 (70), 253 (3), 236 (24), and 208 (6).

Reaction of 1-t-Butylpyrano[3,4-b]indol-3-one (**1h**) *with Ethyl Propiolate.*—A mixture of the pyranoindole (**1h**) (46 mg, 0.19 mmol) and ethyl propiolate (75 mg, 0.76 mmol) in bromobenzene (15 ml) was refluxed under nitrogen for 12 h. The mixture was evaporated and the residue chromatographed to give ethyl 1-t-butyl-9H-carbazole-3-carboxylate (**8h**) (28 mg, 50%), m.p. 209—211 °C (Found: C, 77.2; H, 7.2; N, 4.7. $C_{19}H_{21}NO_2$ requires C, 77.3; H, 7.2; N, 4.7%); $v_{max.}$(Nujol) 3 390, 3 350sh, 1 680, 1 600, 1 255, and 750 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.46 (3 H, t, J 7.0 Hz), 1.59 (9 H, s), 4.45 (2 H, q, J 7.0 Hz), 7.29 (1 H, ~t, J 7.9 Hz), 7.43—7.54 (2 H, m), 8.10 (1 H, s, 2-H), 8.13 (1 H, d, J 7.5 Hz, 5-H), 8.39 (1 H, br, NH), and 8.70 (1 H, s, 4-H); m/z 295 (M^+, 73%), 280 (100), 250 (12), and 234 (4).

Reaction of Ethyl 1-Methyl-3-oxopyrano[3,4-b]indole-9-carboxylate (**10**) *with Ethyl Propiolate.*—A mixture of the pyranoindolone (**10**) (50 mg, 0.18 mmol) and ethyl propiolate (88 mg, 0.90 mmol) in bromobenzene (4 ml) was heated under reflux for 24 h. The mixture was evaporated, and the residue chromatographed to give diethyl 1-methyl-9H-carbazole-2,9-dicarboxylate (**12**) and diethyl 1-methyl-9H-carbazole-3,9-dicarboxylate (**11**) (1.4:1; 52 mg, 86%); δ_H(250 MHz; CDCl$_3$) 1.40—1.54 (m, ethoxy CH$_3$, both isomers), 2.56 (3 H, s, CH$_3$ minor), 2.67 (3 H, s, CH$_3$ major), 4.37—4.60 (m, OCH$_2$, both isomers), 7.34—7.42 (m), 7.46—7.55 (m), 7.82 (1 H, d, J 7.8 Hz, major), 7.93—8.05 (m), 8.09—8.15 (m), and 8.52 (1 H, s, minor).

The mixture of carbazoles (**11**) and (**12**) (50 mg) was dissolved in ethanol (5 ml) and treated with sodium ethoxide (50 mg). The mixture was stirred at room temperature under nitrogen for 24 h, acidified with dilute hydrochloric acid, poured into brine (10 ml), and extracted with ether (20 ml). The ether extract was dried (MgSO$_4$) and evaporated to give a mixture of ethyl 1-methyl-9H-carbazole-2-carboxylate (**9b**) and ethyl 1-methyl-9H-carbazole-3-carboxylate (**8b**) (1.3:1; 38 mg, 98%).

Reaction of the Pyranoindolone (**1b**) *with Unsymmetrical Acetylenes*

Reaction of the Pyranoindolone (**1b**) *with Methyl Propiolate.*—This reaction has been described previously,[1] and gave the carbazoles (**13a**) and (**14a**) (1:1; 84%).

Reaction of 1-Methylpyrano[3,4-b]indol-3-one (**1b**) *with Hex-1-yn-3-one.*—A mixture of the pyranoindole (**1b**) (414 mg, 2.08 mmol) and hex-1-yn-3-one (988 mg, 10.29 mmol) in bromobenzene (30 ml) was heated under reflux for 3 h. The mixture was evaporated and the residue chromatographed to give 2-butyryl-1-methyl-9H-carbazole (**14b**) and 3-butyryl-1-methyl-9H-carbazole (**13b**) (1:2.8; 463 mg, 87%). The two isomers were not separable by column chromatography and were therefore characterised as a mixture (Found: C, 81.35; H, 6.8; N, 5.6. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); $v_{max.}$(Nujol) 3 298br, 1 658, 1 600, 1 190, 1 230, and 736 cm^{-1}; δ_H[250 MHz; (CD$_3$)$_2$SO] 0.90—0.99 (2 × t, J 7 Hz, propyl CH$_3$, both isomers), 1.57—1.76 (m, CH$_2$, both isomers), 2.58 (3 H, s, CH$_3$, major), 2.62 (3 H, s, CH$_3$, minor), 2.98 (2 H, t, J 7.5 Hz, minor), 3.08 (2 H, t, J 7.5 Hz, major), 7.14—7.25 (m, both isomers), 7.93—7.45 (~t, J 8.1 Hz), 7.51—7.56 (m), 7.83 (1 H, s, major), 8.03 (1 H, d, J 8.1 Hz, minor), 8.15 (1 H, d, J 8.1 Hz, minor), 8.24 (1 H, d, J 8.1 Hz, major), 8.7 (1 H, s, major), and 11.22 (1 H, br, major), and 11.39 (1 H, br, minor); m/z 251 (M^+, 36%), 208 (100), 180 (27), and 152 (6).

Reaction of 1-Methylpyrano[3,4-b]indol-3-one (**1b**) *with Phenylacetylene.*—A mixture of the pyranoindole (**1b**) (340 mg, 1.7 mmol) and phenylacetylene (524 mg, 5.1 mmol) in bromobenzene (75 ml) was heated at reflux under nitrogen for 120 h. The solvent was evaporated and the residue chromatographed to give 1-methyl-3-phenyl-9H-carbazole (**13c**) as a white solid (204 mg, 32%), m.p. 128—129 °C (Found: C, 88.7; H, 5.9; N, 5.4. $C_{19}H_{15}N$ requires C, 88.7; H, 5.9; N, 5.4%); $v_{max.}$(Nujol) 3 420, 1 600, 1 240, 870, 765, 750, 736, and 700 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 2.61 (3 H, s), 7.22—7.51 (7 H, m), 7.68—7.74 (2 H, m), 7.97 (1 H, br), 8.1 (1 H, d, J 7.5 Hz), and 8.14 (1 H, s); m/z 257 (M^+, 100%), 180 (4), and 128 (16).

Reaction of 1-Methylpyrano[3,4-b]indol-3-one (**1b**) *with Hept-1-yne.*—A mixture of the pyranoindole (**1b**) (500 mg, 2.5 mmol) and hept-1-yne (954 mg, 10 mmol) in bromobenzene (75 ml) was heated at reflux under nitrogen for 72 h. The mixture was evaporated and the residue chromatographed to give 1-methyl-3-pentyl-9H-carbazole (**13d**) as a white solid (100 mg, 16%), m.p. 89.5—91 °C (Found: C, 85.8; H, 8.6; N, 5.6. $C_{18}H_{21}N$ requires C, 86.0; H, 8.4; N, 5.6;); $v_{max.}$(Nujol) 3 405, 1 600, and 750 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 0.94 (3 H, t, J 6.5 Hz), 1.33—1.43 (4 H, m), 1.67—1.79 (2 H, m), 2.55 (3 H, s), 2.77 (2 H, t, J 8.0 Hz), 7.09 (1 H, s), 7.23 (1 H, ~t, J 7.5 Hz), 7.36—7.47 (2 H, m), 7.75 (1 H, s), 7.87 (1 H, br), and 8.05 (1 H, d, J 7.5 Hz); m/z 251 (M^+, 33%), and 194 (100).

Reaction of 1-Methylpyrano[3,4-b]indol-3-one (**1b**) *with 3,3-Dimethylbut-1-yne.*—A mixture of the pyranoindole (**1b**) (257 mg, 1.29 mmol) and 3,3-dimethylbut-1-yne (813 mg, 9.9 mmol) in THF (12 ml) was heated in a sealed tube at 200 °C for 48 h. The mixture was evaporated and the residue chromatographed to give 1-methyl-3-t-butyl-9H-carbazole (**13e**) as the only product by 250 MHz n.m.r. (23.6 mg, 8%), m.p. 106—110 °C (Found: M^+, 237.1513. $C_{17}H_{19}N$ requires M, 237.1517); $v_{max.}$(CHCl$_3$) 3 480, 1 605, 1 364, 1 335, 1 308, and 870 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.47 (9 H, s), 2.59 (3 H, s), 7.20—7.27 (1 H, m), 7.33 (1 H, s), 7.37—7.48 (2 H, m), 7.89 (1 H, br, NH), 7.96 (1 H, s, 4-H), 8.10 (1 H, d, J 8 Hz, 5-H); m/z 237 (M^+, 38%), 222 (100), 206 (7), 194 (6), and 180 (7).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl But-2-ynoate*.—A mixture of the pyranoindole (**1b**) (413 mg, 2.08 mmol) and methyl but-2-ynoate (814 mg, 8.3 mmol) in bromobenzene (30 ml) was refluxed under nitrogen for 36 h. The mixture was evaporated and the residue chromatographed to give *methyl* 1,2-*dimethyl-9H-carbazole-3-carboxylate* (**13f**) (31 mg, 6%), m.p. 206—208 °C (Found: M^+, 253.1101. $C_{16}H_{15}NO_2$ requires M, 253.1103); $v_{max.}$(CHCl$_3$) 3 480, 1 705, 1 612, and 1 350 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 2.49 (3 H, s), 2.66 (3 H, s), 3.93 (3 H, s), 7.20—7.27 (1 H, m), 7.36—7.47 (2 H, m), 8.03 (1 H, d, J 7.8 Hz), 8.05 (1 H, br), and 8.50 (1 H, s, 4-H); m/z 253 (M^+, 100%), 238 (8), 222 (69), 194 (37), 193 (40), and 180 (5); and *methyl* 1,3-*dimethyl-9H-carbazole-2-carboxylate* (**14f**) (157 mg, 30%), m.p. 110—112 °C (Found: M^+, 253.1088. $C_{16}H_{15}NO_2$ requires M, 253.1103); $v_{max.}$(CHCl$_3$) 3 480, 1 720, 1 340, 1 285, and 1 134 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 2.46 (3 H, s), 2.49 (3 H, s), 3.97 (3 H, s), 7.19—7.24 (1 H, m), 7.38—7.40 (2 H, m), 7.72 (1 H, s, 4-H), 8.01 (1 H, d, J 8 Hz, 5-H), and 8.11 (1 H, br, NH); m/z 253 (M^+, 100%), 238 (6), 222 (37), 208 (3), 194 (34), 193 (52), and 180 (4).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Hept-2-yn-3-one*.—A mixture of the pyranoindole (**1b**) (328 mg, 1.65 mmol) and hept-2-yn-3-one (712 mg, 6.47 mmol) in bromobenzene (20 ml) was heated at reflux under nitrogen for 24 h. The mixture was evaporated and the residue chromatographed to give 2-*butyryl*-1,3-*dimethyl-9H-carbazole* (**14g**) and 3-*butyryl*-1,2-*dimethyl-9H-carbazole* (**13g**) (3:1) (182 mg, 42%). The isomers were characterised as a mixture (Found: C, 81.6; H, 7.4; N, 5.2. $C_{18}H_{19}NO$ requires C, 81.5; H, 7.2; N, 5.3%); $v_{max.}$(Nujol) 3 340, 1 692, 1 254, 880, 775, 759, and 744 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.03 (t, J 7.6 Hz, CH$_2$CH$_3$, both isomers), 1.69—1.87 (m, CH$_2$CH$_2$, both isomers), 2.36 (3 H, s, major), 2.38 (3 H, s, major), 2.41 (3 H, s, minor), 2.52 (3 H, s, minor), 2.76 (2 H, t, J 7.6 Hz, COCH$_2$, major), 3.01 (2 H, t, J 7.6 Hz, COCH$_2$, minor), 7.17—7.27 (m, both isomers), 7.37—7.41 (m, both isomers), 7.70 (1 H, s, 4-H, major), 8.00 (1 H, d, J 7.5 Hz, 5-H, major), 8.03 (1 H, d, J 7.5 Hz, 5-H, minor), 8.10 (1 H, br, NH, major), 8.14 (1 H, s, 4-H, minor), and 8.26 (1 H, br, NH, minor); m/z 265 (M^+, 35%), 222 (100), and 194 (22).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl Phenylpropiolate*.—A mixture of the pyranoindole (**1b**) (200 mg, 1 mmol) and methyl phenylpropiolate (296 mg, 2 mmol) in bromobenzene (50 ml) was heated under reflux for 72 h. The mixture was evaporated and the residue chromatographed to give *methyl* 1-*methyl-2-phenyl-9H-carbazole-3-carboxylate* (**13h**) (53 mg, 17%), m.p. 181—182 °C (Found: C, 79.8; H, 5.5; N, 4.5. $C_{21}H_{17}NO_2$ requires C, 80.0; H, 5.4; N, 4.4%); $v_{max.}$(Nujol) 3 330, 1 695, 1 344, 1 242, and 730 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 2.27 (3 H, s), 3.63 (3 H, s), 7.21—7.51 (8 H, m), 8.12 (1 H, d, J 7.7 Hz) 8.21 (1 H, br), and 8.60 (1 H, br); m/z 315 (M^+, 100%), 284 (56), 269 (14), and 254 (23); and *methyl* 1-*methyl-3-phenyl-9H-carbazole-2-carboxylate* (**14h**) (181 mg, 57%), m.p. 149—150 °C (Found: C, 79.75; H, 5.3; N, 4.5. $C_{21}H_{17}NO_2$ requires C, 80.0; H, 5.4; N, 4.4%); $v_{max.}$(Nujol) 3 300, 1 702, 1 290, 1 270, 1 135, 754, and 740 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 2.61 (3 H, s), 3.63 (3 H, s), 7.23—7.51 (8 H, m), 7.96 (1 H, s), 8.08 (1 H, d, J 8 Hz), and 8.22 (1 H, br); m/z 315 (M^+, 100%), 284 (36), 269 (12), 254 (22), and 241 (14).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl Hex-2-ynoate*.—A mixture of the pyranoindole (**1b**) (274 mg, 1.38 mmol) and methylhex-2-ynoate (733 mg, 5.82 mmol) in bromobenzene (30 ml) was heated under reflux for 24 h. The mixture was evaporated and the residue chromatographed to give *methyl* 1-*methyl-2-propyl-9H-carbazole-3-carb-oxylate* (**13i**) (12 mg, 3%). m.p. 80—85 °C (Found: M^+, 281.1417. $C_{18}H_{19}NO_2$ requires M, 281.1416); $v_{max.}$(CHCl$_3$)

3 470, 1 710, 1 605, and 1 340 cm^{-1}; δ_H[250 MHz; (CD$_3$)$_2$CO] 1.02 (3 H, t, J 6.8 Hz), 1.55—1.70 (2 H, m), 2.57 (3 H, s), 3.10 (2 H, ~t, J 8 Hz, benzylic CH$_2$), 3.87 (3 H, s), 7.19 (1 H, ~t, J 8 Hz), 7.39 (1 H, ~t, J 8 Hz), 7.51 (1 H, d, J 8 Hz, 8-H), 8.12 (1 H, d, J 8 Hz, 5-H), 8.51 (1 H, s), and 10.52 (1 H, br); m/z 281 (M^+, 80%), 252 (100), 250 (25), and 222 (7); and *methyl* 1-*methyl-3-propyl-9H-carbazole-2-carboxylate* (**14i**) (116 mg, 30%), m.p. 139—140 °C (Found: C, 76.9; H, 6.8; N, 5.0. $C_{18}H_{19}NO_2$ requires C, 76.8; H, 6.8; N, 5.0%); $v_{max.}$(Nujol) 3 355, 1 704, 1 270, and 750 cm^{-1}; δ_H(250 MHz; CDCl$_3$ 0.99 (3 H, t, J 7.3 Hz), 1.63—1.79 (2 H, m, CH$_2$), 2.50 (3 H, s, CH$_3$), 2.75 (2 H, t, J 7 Hz), 3.98 (3 H, s), 7.20—7.26 (1 H, m), 7.41—7.44 (2 H, m), 7.78 (1 H, s), 8.03 (1 H, br), and 8.05 (1 H, d, J 7.9 Hz); m/z 281 (M^+, 69%), 252 (100), and 222 (9).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl t-Butylpropiolate*.—A mixture of the pyranoindole (**1b**) (300 mg, 1.51 mmol) and methyl t-butylpropiolate (633 mg, 4.5 mmol) in bromobenzene (50 ml) was heated at reflux under nitrogen for 72 h. The mixture was evaporated and the residue chromatographed to give *methyl* 1-*methyl-3-t-butyl-9H-carb-azole-2-carboxylate* (**14j**) (126 mg, 28%), m.p. 130—132 °C (Found: C, 77.1; H, 7.1; N, 4.7. $C_{19}H_{21}NO_2$ requires C, 77.3; H, 7.2; N, 4.7%); $v_{max.}$(Nujol) 3 360, 3 420, 1 738, 1 699, 1 260, and 750 cm^{-1}; $v_{max.}$(CHCl$_3$) 3 480, 1 720, 1 230br, 1 150, and 1 128 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.52 (9 H, s), 2.43 (3 H, s), 3.96 (3 H, s), 7.20—7.30 (1 H, m), 7.39—7.45 (2 H, m), 8.01 (1 H, br), 8.06 (1 H, s), and 8.09 (1 H, d, J 8.1 Hz); m/z 295 (M^+, 89%), 280 (86), 248 (100), 220 (9), and 205 (17).

Reaction of 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl 4-Hydroxyhept-2-ynoate*.—A mixture of the pyrano-indole (**1b**) (102 mg, 0.51 mmol) and methyl 4-hydroxyhept-2-ynoate (240 mg, 1.54 mmol) in bromobenzene (8 ml) was heated at reflux under nitrogen for 16 h. The mixture was evaporated and the residue chromatographed to give 4-*methyl-1-propyl-5H-furo*[3,4-b]*carbazol-3-one* (**15**) (91 mg, 64%), m.p. 229—232 °C (Found: C, 77.2; H, 6.1; N, 4.95. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $v_{max.}$(Nujol) 3 280br, 1 725, 1 629, 1 506, 1 251, 1 182, and 750 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.00 (3 H, t, J 7 Hz), 1.45—1.67 (2 H, m), 1.70—1.89 (1 H, m), 2.04—2.18 (1 H, m), 2.95 (3 H, s), 5.52—5.18 (1 H, m), 7.25—7.34 (1 H, m), 7.48—7.56 (2 H, m), 7.87 (1 H, s, 10-H), 8.11 (1 H, d, J 7.8 Hz, 9-H), and 8.33 (1 H, br); m/z 279 (M^+, 38%), 236 (100), 208 (19), 180 (14), 44 (88), and 28 (85).

Reaction at 1-*Methylpyrano*[3,4-b]*indol-3-one* (**1b**) *with Methyl 4-Oxohept-2-ynoate*.—A mixture of the pyranoindole (**1b**) (61 mg, 0.31 mmol) and methyl 4-oxohept-2-ynoate (171 mg, 1.11 mmol) in bromobenzene (8 ml) was heated at reflux under nitrogen for 3 h. The mixture was evaporated and the residue chromatographed (ether–light petroleum) to give *methyl* 2-*butyryl-1-methyl-9H-carbazole-3-carboxylate* (**13l**) (41 mg, 43%), m.p. 179—182 °C (Found: C, 73.5; H, 6.2; N, 4.5. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.2; N, 4.5%); $v_{max.}$(Nujol) 3 360br, 1 710sh, 1 690, 1 350, 1 248, and 1 012 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.03 (3 H, t, J 7.7 Hz), 1.77—1.92 (2 H, m), 2.40 (3 H, s), 2.76 (2 H, t, J 7.7 Hz), 3.92 (3 H, s), 7.16—7.24 (1 H, m), 7.34—7.39 (2 H, m), 8.08 (1 H, d, J 7.2 Hz), 8.48 (1 H, br, NH), and 8.60 (1 H, s, 4-H); m/z 309 (M^+, 17%), 278 (4), and 266 (100), and *methyl* 3-*butyryl-1-methyl-9H-carbazole-2-carboxy-late* (**14l**) (48 mg, 50%), m.p. 155—157 °C (Found: C, 73.6; H, 6.2; N, 4.5. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.2; H, 4.5%); $v_{max.}$(Nujol) 3 396, 1 711, 1 671, 1 570, 1 256, 1 140, and 752 cm^{-1}; δ_H(250 MHz; CDCl$_3$) 1.00 (3 H, t, J 7.6 Hz), 1.68—1.83 (2 H, m), 2.41 (3 H, s), 2.91 (2 H, t, J 7.6 Hz), 3.97 (3 H, s), 7.24—7.33 (1 H, m), 7.41—7.44 (2 H, m), 8.02 (1 H, d, J 7.9 Hz), 8.20 (1 H, s, 4-H), and 8.63 (1 H, br, NH); m/z 309 (M^+, 20%), 278 (8), and 266 (100).

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