Diels–Alder Reactivity of Pyrano[4,3-*b*]indol-3-ones, Indole 2,3-Quinodimethane Analogues

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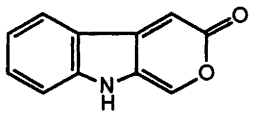
The pyrano[4,3-*b*]indol-3-ones (**7**) are stable indole-2,3-quinodimethane type dienes, which undergo Diels–Alder reaction with alkynes to give, after loss of carbon dioxide, carbazoles. The reactivity of the diene is increased by the presence of the electron-withdrawing t-butoxycarbonyl group on the indole nitrogen. The pyranoindolones (**7**) are less reactive, and exhibit the opposite regiochemistry in their Diels–Alder reactions than the isomeric pyrano[3,4-*b*]indol-3-ones (**1**). Factors which affect the regiochemistry of the Diels–Alder reaction are discussed.

Over the last 5 years we have been interested in the synthesis and Diels–Alder reactivity of the pyrano[3,4-*b*]indol-3-one system (**1**), stable compounds which contain the indole-2,3-quinodimethane diene. Thus we have described their cycloaddition to simple alkynes to give, after loss of carbon dioxide, carbazoles,[1] and the steric and electronic factors which influence the regioselectivity of the Diels–Alder reaction.[2] We have also described intramolecular Diels–Alder reactions,[3] and the use of pyrano[3,4-*b*]indol-3-ones in the synthesis of the carbazole alkaloids carbazomycin A and B, and hyellazole.[4] It was, therefore, of interest to investigate the isomeric pyrano[4,3-*b*]indol-3-one diene system (**2**) and how the reversal of the carbon dioxide bridge would affect the regioselectivity of the Diels–Alder reaction.



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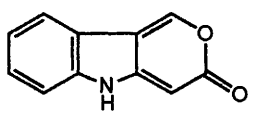
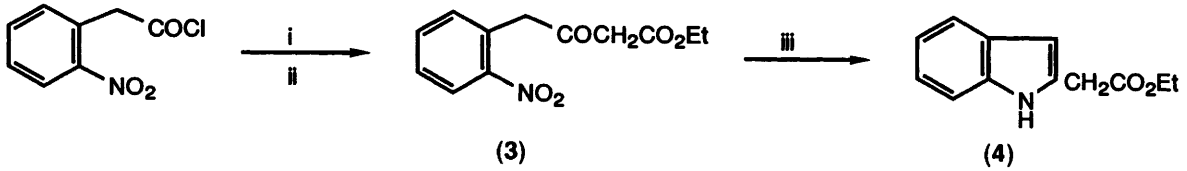


(2)

Results and Discussion

The pyranoindolone ring system (**1**) is readily prepared from indol-3-ylacetic acid by reaction with acid anhydrides in the presence of boron trifluoride–diethyl ether,[1,4] and therefore the most likely precursor to the isomeric pyranoindolone (**2**) would be indol-2-ylacetic acid. However, unlike the 3-isomer, indol-2-ylacetic acid is not commercially available. Although there are routes to indol-2-ylacetic acid based on the modification of other indoles, for example, from 1-phenylsulphonylindole,[5,6] from indole-2-carboxylic acid,[7] or from 2-methylindole,[8] we elected to use a ring synthesis based on the reductive cyclisation of ethyl 4-(2-nitrophenyl)acetoacetate (**3**). In the original method,[9] the β-keto ester (**3**) was prepared by reaction of 2-nitrophenylacetyl chloride with the anion of ethyl acetoacetate, followed by treatment with ammonia. We employed a more modern route to β-keto esters based on Meldrum's acid.[10] Thus acylation of Meldrum's acid with 2-nitrophenylacetyl chloride in the presence of *N,N*-di-isopropylethylamine gave the *C*-acylated Meldum's acid, ethanolysis of which gave the required β-keto ester (**3**) in 85% overall yield. It is interesting to note that the use of pyridine as base, as recommended in the original procedure for a variety of acid chlorides,[10] results, in the case of 2-nitrophenylacetyl chloride, in a very poor yield of β-keto ester, and therefore our modification using Hunig's base was necessary. Reductive cyclisation of the β-keto ester (**3**) using titanium(III) chloride in aqueous acetone gave ethyl indol-2-ylacetate (**4**) in 75% yield (Scheme 1).

Although the ester (**4**) was readily hydrolysed, the subsequent reaction of indol-2-ylacetic acid with acetic anhydride in the presence of boron trifluoride–diethyl ether to give 1-methylpyrano[4,3-*b*]indol-3-one (**7b**) was unsatisfactory. Therefore an alternative approach was used (Scheme 2). The ester (**4**) was treated with *N*-methylformanilide and phosphorus oxychloride in 1,2-dichloroethane to give the 3-formylindole (**5a**) (66%), hydrolysis of which gave 3-formylindol-2-ylacetic acid (**6a**) in quantitative yield. Reaction of the formyl acid (**6a**) with acetic anhydride at room temperature resulted in cyclodehydration to give the unsubstituted pyrano[4,3-*b*]indol-3-one (**7a**) in 90% yield. Similarly, the ester (**4**) could be acetylated using acetyl chloride in the presence of tin(IV) chloride to give ethyl 3-acetylindol-2-ylacetate (**5b**), which was converted into the pyranoindolone (**7b**) by hydrolysis and cyclodehydration as above. Finally, in order to investigate the effect, if any, of the free NH group on the Diels–Alder reactivity of the indole-2,3-quinodimethane diene system, both pyrano[4,3-*b*]indolones (**7**) were converted into the corresponding *N*-t-butoxycarbonyl (Boc) derivatives (**8**) by reaction with di-t-butyl oxydiformate.



(3) (4)

Scheme 1. *Reagents:* i, Meldrum's acid, Pr^i_2NEt, CH_2Cl_2; ii, EtOH, reflux; iii, $TiCl_3$, acetone, ammonium acetate buffer.

The pyranoindolones (**7**) and (**8**) are stable solids which show the expected spectroscopic properties, although nuclear Overhauser effect (NOE) difference spectroscopy was used to assign the ^1H NMR spectrum of the parent pyranoindolone (**7a**). Thus, pre-irradiation of the broad singlet at δ 10.2 (NH)

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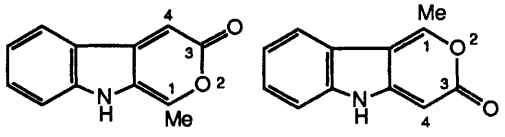
Scheme 2. (**a**, R = H; **b**, R = Me) *Reagents*: i, $PhNMeCHO$, $POCl_3$, $ClCH_2CH_2Cl$ (R = H) or AcCl, $SnCl_4$, CH_2Cl_2 (R = Me); ii, KOH, aqueous THF–MeOH; iii, Ac_2O, THF; iv, $(Boc)_2O$, NaH, DMF.

caused enhancements of the singlet at δ 5.61 (4-H) and the doublet at δ 7.23 (5-H). However, there are important differences between the spectra of this ring system (**2**) and the isomeric pyrano[3,4-*b*]indol-3-ones (**1**), as illustrated by the comparison between the methyl substituted compounds (**1a**) and (**7b**). Thus, the carbonyl absorptions in their IR spectra occur at 1 695 and 1 681 cm^{-1} respectively, and the proton adjacent to the carbonyl group (4-H in both compounds) resonates at δ 6.43 and 5.46 respectively in their ^1H NMR spectra. In the ^{13}C NMR spectra, which were assigned by using gated broad-band decoupling, the pyrone (**1a**) shows resonances for C-4 and C-1 at δ 95.5 and 144.3 respectively. The corresponding resonances in pyrone (**7b**) occur at δ 79.8 and 159.0. These observations are consistent with a decrease in carbonyl double-bond character of the pyrone (**7b**) compared with its isomer (**1a**).



The pyranoindolones (**7**) and (**8**) undergo Diels–Alder reaction with a variety of alkynes on being heated in refluxing chlorobenzene to give, after loss of carbon dioxide, the carbazoles (**9**) and/or (**10**). In the case of the NBoc pyranoindolones (**8a**, **b**), competition occurs between cycloaddition to the alkyne and thermal removal of the Boc group from the starting pyranoindolone. Results are further complicated by the partial removal of the Boc group from the product carbazoles. The results are summarised in Table 1, and when taken in combination with the corresponding results obtained from the Diels–Alder reactions of the isomeric pyrano[3,4-*b*]indol-3-ones several interesting points emerge.

Reactivity.—The more electron-deficient alkynes react faster, suggesting that the Diels–Alder reactions of the pyrano[4,3-*b*]indol-3-one diene system (**2**), like the [3,4-*b*] isomer (**1**), are 'normal' electron demand. However, the pyranoindolones (**2**) are less reactive than the isomeric pyranoindolones (**1**), and within the series of dienes (**7**) and (**8**), the reactivity increases in the order: 1-methyl, NH (**7b**) < 1-H, NH (**7a**) < 1-H, NBoc (**8a**) (Table 1, Entries 1–3). We attribute this to the effect of the substituents on the degree of aromatic character of the pyran-2-one ring. Thus in the [3,4-*b*] series, the aromatic tautomer can be stabilised by the inductive effect of an alkyl substituent R, although the nitrogen lone pair has no stabilising effect. However, in the present work, the aromatic tautomer is stabilised by both the inductive effect of the methyl group and by the nitrogen lone pair. Placing an electron-withdrawing group (Boc) on nitrogen dramatically increases the diene reactivity of the pyrano[4,3-*b*]indolone ring. These effects are borne out in the IR spectra of the pyranoindolones (**7a**) and (**8a**) which show carbonyl frequencies at 1 681 and 1 708 cm^{-1}, and NMR signals for 4-H at δ 5.61 and 6.65 respectively.

Regioselectivity.—Propiolic esters are unusual in their Diels–Alder reactions with 2-pyrones in that, in contrast to many other alkynes, they exhibit little or no regioselectivity.[11] This is borne out in the present case where the pyranoindolones (**7**) and (**8**) give approximately equal amounts of the carbazole-2- and 3-esters (**9**) and (**10**) on reaction with ethyl propiolate (Table 1, Entries 4–6). These results parallel those found with the isomeric pyrano[3,4-*b*]indol-3-ones, which, in the absence of steric factors, exhibit little regioselectivity in their reactions with ethyl propiolate, although there is a slight preference for the formation of carbazole 3-esters.[2]

The reactions of the pyranoindolones (**7a**), (**7b**), and (**8b**) with methyl tetrolate and with ethyl trimethylsilylpropynoate respectively (Table 1, Entries 10, 11, and 12) gave no detectable carbazole products even after prolonged heating. However, on reaction with methyl phenylpropiolate and with ethyl trimethylsilylpropynoate the pyrano[4,3-*b*]indol-3-ones (**7a**) and (**8a**) undergo regioselective Diels–Alder reaction to give the carbazole 3-esters (**10**) as the only detectable carbazole products (Table 1, Entries, 7, 8, and 9). The structure of the carbazole (**10i**) was proved by NOE difference spectroscopy in which pre-irradiation of the singlet at δ 7.86 (1-H) caused enhancements of the singlet at 0.36 ($SiMe_3$) and the broad singlet at 10.65 (NH). The structure was further confirmed by proto-desilylation to give the known ethyl carbazole-3-carboxylate (**10d**).

In contrast, the isomeric pyrano[3,4-*b*]indol-3-ones give carbazole 2-esters as the major or sole products on reaction

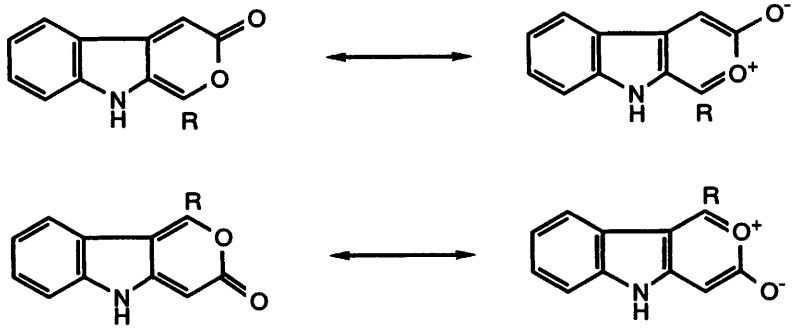
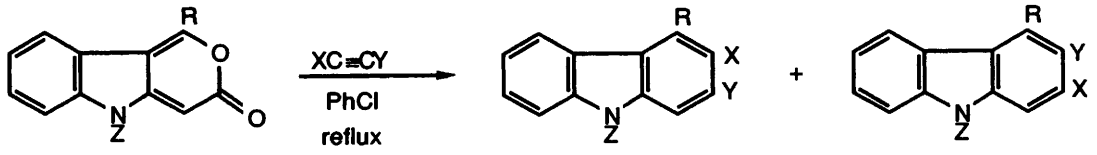


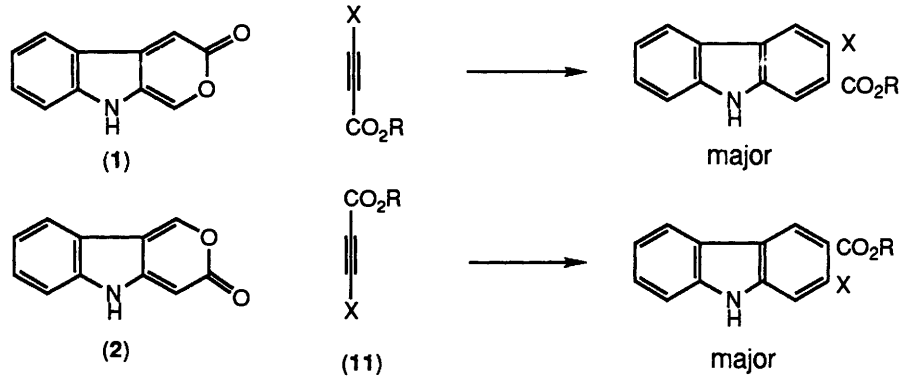
Table 1. Diels–Alder reactions of the pyrano[4,3-*b*]indol-3-ones (7) and (8) with alkynes



(7)/(8) (9) (10)

Entry	R	Z	X	Y	Time (h)	(9)/(10)	Combined yield (%)	Ratio (9):(10)
1	H	H	CO_2Me	CO_2Me	44	**a**	92	—
2	H	Boc	CO_2Me	CO_2Me	20	**b**	82	*a*
3	Me	H	CO_2Me	CO_2Me	144	**c**	30	—
4	H	H	H	CO_2Et	167	**d**	90	1:1.2
5	H	Boc	H	CO_2Et	25	**e**	62	1.5:1[b]
6	Me	H	H	CO_2Et	425	**f**	78	1:2
7	H	H	Ph	CO_2Me	241	**g**	28	1:>20[c,d]
8	H	Boc	Ph	CO_2Me	48	**h**	40	1:>20[d,e]
9	H	H	$SiMe_3$	CO_2Et	262	**i**	24	1:>20[d]
10	H	H	Me	CO_2Me	528		0	—
11	Me	H	$SiMe_3$	CO_2Et	1 344		0	—
12	Me	Boc	$SiMe_3$	CO_2Et	96		0	*f*

[a] A mixture of NBoc and NH carbazoles was formed; this mixture was heated neat to give only the NH carbazole. [b] A mixture of NBoc (10%) and NH (52%) carbazoles was formed; *ca.* 35% NH pyranoindolone recovered. [c] Carried out in PhBr at 140 °C. [d] Only a single carbazole product observed by 270 MHz ^{1}H NMR. [e] *ca.* 60% of NH pyranoindolone recovered. [f] *ca.* 85% of NH pyranoindolone recovered.



Scheme 3.

with the same alkynes,[2,4] and this difference in regioselectivity between the isomeric dienes (**1**) and (**2**) is summarised in general in Scheme 3. We have also observed a similar difference in the regioselectivity of the Diels–Alder reaction of benzothieno[2,3-*c*]pyran-3-ones and their [3,2-*c*]-fused isomers.[12]

The regioselectivity of the Diels–Alder reactions of the pyranoindolones (**1**) and (**2**) with acetylenic esters (**11**; X not H) is most simply explained by considering the 'directing effect' of the pyrone ring oxygen atom. In the case of the [3,4-*b*] isomer (**1**), this effect must dominate any electron release from the nitrogen atom, and hence the Diels–Alder reaction proceeds as shown. In the isomeric pyrano[4,3-*b*]indolones (**2**) the directing effect of the pyrone ring oxygen is reinforced by any electron release from nitrogen, and hence the regioselectivity should, if anything, be greater, but opposite to that observed with pyranoindolone (**1**), since the oxygen atom is attached to the opposite terminus of the diene. Although we do not have enough results to comment on the degree of regioselectivity of the two pyranoindolone dienes, the fact that they exhibit opposite regioselectivity seems clear.

Experimental

270 MHz ^{1}H NMR and 67.9 MHz ^{13}C NMR spectra were obtained on a JEOL GSX 270 spectrometer, and UV spectra were obtained on a Philips PU8740 UV/VIS scanning spectrophotometer; for other general points, see ref. 2.

1-*Methylpyrano*[3,4-b]*indol-3-one* (**1a**).—For preparation, see reference 2; λ_{max}(tetrahydrofuran) 243 (ε 29 329), 273 (17 622), 435 (7 195), and 462 nm (7 622); δ_C(67.9 MHz; $(CD_3)_2SO$) 16.4 (q, J_{CH} 130 Hz, CH_3), 95.5 (d, J_{CH} 171 Hz, 4-C), 111.3 (dd, J_{CH} 166 Hz, $^2J_{CH}$ 8 Hz, aromatic C), 118.9 (dd, J_{CH} 162 Hz, $^2J_{CH}$ 7 Hz, aromatic C), 119.3 (m, quaternary C), 124.4 (dd, J_{CH} 162 Hz, $^2J_{CH}$ 8 Hz, aromatic C), 124.9 (quintet, $^2J_{CH}$ 4 Hz, quaternary C), 132.9 (m, aromatic C), 144.3 (q, $^2J_{CH}$ 7 Hz, 1-C), 146.1 (m, quaternary C), 147.9 (m, quaternary C), and 162.5 (d, $^2J_{CH}$ 4 Hz, C=O).

Ethyl 4-(2-*Nitrophenyl*)*acetoacetate* (**3**).—Thionyl chloride (11.5 g, 96.4 mmol) was added to 2-nitrophenylacetic acid (8.72 g, 48.2 mmol) and the suspension was heated to 50 °C and stirred at this temperature until effervescence ceased. The

resulting solution was concentrated under reduced pressure and the residue dissolved in dry dichloromethane (30 ml). This was added dropwise to a stirred solution of Meldrum's acid (6.94 g, 48.2 mmol) and Hunig's base (16.8 ml, 96.4 mmol) in dichloromethane (200 ml) under nitrogen, at 0 °C. After addition was complete, the solution was stirred for 1 h at 0 °C and then allowed to warm to room temperature when it was stirred for a further 1 h. The reaction mixture was poured into a separating funnel and washed, in turn, with dilute hydrochloric acid, water, and brine, and dried ($MgSO_4$). The organic extracts were concentrated under reduced pressure. Absolute ethanol (200 ml) was added to the crude acyl-Meldrum's acid complex and the suspension refluxed until effervescence ceased. The solution was concentrated under reduced pressure and the resulting orange oil triturated with ethanol and left in the freezer overnight. The crude solid was recrystallised from ethanol to give the title compound (**3**) (10.28 g, 85%), as a beige powder, m.p. 55.5–57 °C (lit.,[9] m.p. 56 °C) (Found: C, 57.4; H, 5.0; N, 5.6. Calc. for $C_{12}H_{13}NO_5$: C, 57.4; H, 5,2; N, 5.6%); ν_{max}(Nujol) 1 749 (ester C=O), 1 723 (ketone C=O), 1 613, 1 579, 1 522 (aromatic NO_2), 1 409, 1 347 (aromatic NO_2), 1 308, 1 275, 1 204, 1 152, 1 067, and 1 030 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.33 (3 H, t, *J* 7 Hz, ethoxy CH_3), 3.63 (2 H, s, CH_2COOEt), 4.23 (2 H, q, *J* 7 Hz, ethoxy CH_2), 4.26 (2 H, s, benzyl CH_2), 7.31 (1 H, dd, *J* 8.6 1.6 Hz), 7.48 (1 H, td, *J* 8.6, 8.6, 1.6 Hz), 7.61 (1 H, td, *J* 8.6, 8.6, 1.6 Hz), and 8.14 (1 H, dd, *J* 8.6, 1.6 Hz); *m/z* 251 (M^+, 1.4%), 164(21), 137(45), 120(53), 115(100), 87(32), 43(41), and 29(73).

Ethyl Indol-2-ylacetate (**4**).—Ethyl 4-(2-nitrophenyl)acetoacetate (**3**) (2.68 g, 10.7 mmol) was dissolved in acetone (30 ml) and transferred to a separating funnel. Aqueous ammonium acetate (4M; 288 ml) was added, followed by aqueous titanium(III) chloride (15% w/v; 77 ml). The mixture was shaken for 7 min. The resulting dark green solution was extracted with ether (4 × 100 ml) and the combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed (dichloromethane) to give the title compound (**4**) (1.63 g, 75%), m.p. 28–31 °C; ν_{max}(film) 3 461 (NH), 1 729 (C=O), 1 527, 1 457, 1 220, and 1 029 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7 Hz, ethoxy CH_3), 3.82 (2 H, s, CH_2COOEt), 4.24 (2 H, q, *J* 7 Hz, ethoxy CH_2), 6.36 (1 H, s, 3-H), 7.08 (1 H, t, *J* 8 Hz), 7.16 (1 H, t, *J* 8 Hz), 7.36 (1 H, t, *J* 8 Hz), 7.54 (1 H, d, *J* 8 Hz), and 8.70 (1 H, br, NH); *m/z* 203 (M^+, 45%) and 130(100).

Ethyl 3-Formylindol-2-ylacetate (**5a**).—*N*-Methylformanilide (0.59 ml, 4.79 mmol) and phosphorus oxychloride (0.44 ml, 4.79 mmol) were stirred at room temperature until the yellow Vilsmeier salt precipitated out. 1,2-Dichloroethane (5 ml) was added and the mixture cooled to 0 °C. Ethyl indol-2-ylacetate (885 mg, 4.36 mmol) in 1,2-dichloroethane (20 ml) was added dropwise and the mixture heated to 50 °C and stirred for 0.5 h. After cooling, the mixture was treated with saturated aqueous sodium acetate (25 ml) and extracted with ethyl acetate (4 × 25 ml). The organic extracts were washed with dilute hydrochloric acid, water, and brine, and dried ($MgSO_4$). The solution was concentrated under reduced pressure to yield an orange oil which was triturated with ether to give the *title compound* (**5a**) (665 mg, 66%) as a yellow solid, m.p. 105–107 °C (Found: C, 67.6; H, 5.5; N, 6.1. $C_{13}H_{13}NO_3$ requires C, 67.5; H, 5.7; N, 6.1%); ν_{max}(Nujol) 3 190 (NH), 1 714 (C=O), 1 630, 1 585, 1 499, 1 468, and 1 391 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.34 (3 H, t, *J* 7 Hz, ethoxy CH_3), 4.29 (2 H, q, *J* 7 Hz, ethoxy CH_2), 4.29 (2 H, s, CH_2CO_2Et), 7.28 (2 H, m), 7.42 (1 H, m), 8.16 (1 H, m), 9.86 (1 H, br, NH), and 10.26 (1 H, s, CHO); *m/z* 231 (M^+, 82%), 185(100), 158(83), 130(36), 103(15), 77(17), and 29(18).

Ethyl 3-Acetylindol-2-ylacetate (**5b**).—To a solution of ethyl indol-2-ylacetate (**4**) (517 mg, 2.55 mmol) in dichloromethane (50 ml) at 0 °C, under nitrogen, was added acetyl chloride (0.54 ml, 7.64 mmol), followed by a solution of tin(IV) chloride in dichloromethane (1.0M; 23 ml). The mixture was stirred at room temperature, under nitrogen, for 60 h. Water (50 ml) was added and the mixture extracted with dichloromethane (4 × 50 ml). The organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to give the *title compound* (**5b**) (580 mg, 93%) as a yellow oil (Found: M^+, 245.1059. $C_{14}H_{15}NO_3$ requires 245.1052); ν_{max}($CHCl_3$) 3 397 (NH), 1 729 (ester C=O), 1 642 (α,β-unsaturated ketone C=O), 1 530, 1 489, 1 459, 1 450, 1 375, 1 328, and 1 266 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.20 (3 H, t, *J* 7 Hz, ethoxy CH_3), 2.60 (3 H, s, Ac), 4.12 (2 H, q, *J* J Hz, ethoxy CH_2), 4.27 (2 H, s, CH_2CO_2Et), 7.20 (2 H, m), 7.50 (1 H, m), 8.00 (1 H, m), and 11.26 (1 H, br, NH); *m/z* 245 (M^+, 53%), 203(27), 199(100), 184(25), 171(43), and 130(58).

3-Formylindol-2-ylacetic Acid (**6a**).—Potassium hydroxide solution (2M; 14.4 ml) was added to a solution of ethyl 3-formylindol-2-ylacetate (**5a**) (665 mg, 2.88 mmol) in tetrahydrofuran–methanol (9:1; 30 ml) and stirred at room temperature for 2 h. Water (100 ml) was added and the aqueous mixture extracted with ether (2 × 25 ml). The aqueous phase was acidified (pH 1.5) with dilute hydrochloric acid and extracted with ethyl acetate (4 × 30 ml). These extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to yield the *title compound* (**6a**) (584 mg, 100%), m.p. 138–142 °C (Found: M^+, 203.0581. $C_{11}H_9NO_3$ requires 203.0582); ν_{max}(Nujol) 3 200 (NH), 3 500–2 200br (CO_2H), 1 714 (C=O), 1 617, 1 583, and 1 248 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 4.3 (2 H, s, CH_2CO_2H), 7.2 (2 H, m), 7.5 (1 H, m), 8.2 (1 H, m), 10.3 (1 H, s, CHO), and 11.1 (1 H, br, NH); *m/z* 203 (M^+, 5%), 158(100), 130(29), 103(12), 77(16), and 44(47).

3-Acetylindol-2-ylacetic Acid (**6b**).—Potassium hydroxide solution (2M; 11.8 ml) was added to a solution of ethyl 3-acetylindole-2-ylacetate (**5b**) (580 mg, 2.37 mmol) in tetrahydrofuran–methanol (9:1; 30 ml) and stirred at room temperature for 2 h. Water (100 ml) was added and the aqueous mixture extracted with ether (2 × 25 ml). The aqueous phase was acidified (pH 1.5) with dilute hydrochloric acid and extracted with ethyl acetate (4 × 30 ml). These extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to yield the *title compound* (**6b**) (470 mg, 91%), m.p. 187 °C (decomp.) (Found: C, 66.2; H, 5.1; N, 6.3. $C_{12}H_{11}NO_3$ requires C, 66.35; H, 5.1; N, 6.45%); ν_{max}(Nujol) 3 188 (NH), 3 500–2 300br (CO_2H), 1 718 (C=O), 1 626, 1 544, 1 491, 1 426, 1 328, 1 224, and 1 189 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 2.6 (3 H, s, Ac), 4.3 (2 H, s, CH_2CO_2H), 7.2 (2 H, m), 7.5 (1 H, m), 8.0 (1 H, m), and 11.2 (1 H, br, NH); *m/z* 217 (M^+, 8%), 173(47), 158(100), 130(11), and 77(11).

Pyrano[4,3-b]*indol-3-one* (**7a**).—Acetic anhydride (1 ml) was added to a solution of 3-formylindol-2-ylacetic acid (**6a**) (157 mg, 77 mmol) in tetrahydrofuran (10 ml) and stirred at room temperature for 36 h. The solution was concentrated under reduced pressure and the resulting solid washed with ether and recrystallised from boiling ethyl acetate to give the *title compound* (**7a**) (129 mg, 90%) as a brown powder, m.p. 158 °C (decomp.) (Found: C, 71.1; H, 3.6; N, 7.5. $C_{11}H_7NO_2$ requires C, 71.35; H, 3.8; N, 7.6%); ν_{max}(Nujol) 3 160 (NH), 1 681 (C=O), 1 651, 1 619, 1 587, and 1 207 cm^{-1}; λ_{max}(tetrahydrofuran) 259 (ε 22 263), 269 (30 288), 305 (6 214), 317 (6 091), and 369 nm (2 840); δ_H[270 MHz; $(CD_3)_2CO$] 5.61 (1 H, d, *J* 1 Hz, 4-H), 7.12

(1 H, td, *J* 8, 8 and 1 Hz, 8-H), 7.23 (1 H, d, *J* 8 Hz, 6-H), 7.35 (1 H, td, *J* 8, 8 and 1 Hz, 7-H), 7.82 (1 H, d, *J* 8 Hz, 9-H), 8.51 (1 H, d, *J* 1 Hz, 1-H), and 10.2 (1 H, br, NH); *m/z* 185 (M^+, 100%), 157(27), 129(37), and 126(57).

1-*Methylpyrano*[4,3-b]*indol*-3-*one* (**7b**).—Acetic anhydride (1 ml) was added to a solution of 3-acetylindol-2-ylacetic acid (**6b**) (370 mg, 1.71 mmol) in tetrahydrofuran (10 ml) and stirred at room temperature for 36 h. The solution was concentrated under reduced pressure and the resulting solid washed with ether and recrystallised from boiling ethyl acetate to give the *title compound* (**7b**) (236 mg, 70%) as a brown powder, m.p. 216 °C (decomp.) (Found: C, 72.05; H, 4.5; N, 6.9. $C_{12}H_9NO_2$ requires C, 72.35; H, 4.55; N, 7.0%); ν_{max}(Nujol) 3 148 (NH), 1 681 (C=O), 1 642, 1 619, and 1 587 cm^{-1}; λ_{max}(tetrahydrofuran) 259 (ε 41 436), 269 (55 479), 306 (10 053), 319 (13 298), 367 (4 681), and 386 nm (3 404); δ_H[270 MHz; $(CD_3)_2CO$] 2.68 (3 H, s, Me), 5.46 (1 H, s, 4-H), 7.14 (1 H, td, *J* 7, 7, and 1 Hz), 7.23 (1 H, dd, *J* 8 and 1 Hz), 7.33 (1 H, td, *J* 8, 8, and 1 Hz), 7.77 (1 H, d, *J* 7 Hz), and 10.13 (1 H, br, NH); δ_C[67.9 MHz; $(CD_3)_2SO$] 18.8 (q, J_{CH} 130 Hz CH_3), 79.8 (d, J_{CH} 168 Hz, 4-C), 110.2 (m, quaternary C), 110.7 (dd, J_{CH} 162 Hz, $^2J_{CH}$ 8 Hz, aromatic C), 120.9 (m, quaternary C), 121.2 (dd, J_{CH} 162 Hz, $^2J_{CH}$ 7 Hz, aromatic C), 121.7 (dd, J_{CH} 161 Hz, $^2J_{CH}$ 9 Hz, aromatic C), 127.6 (dd, J_{CH} 162 Hz, $^2J_{CH}$ 8 Hz, aromatic C), 142.9 (td, $^2J_{CH}$ 7, 7 and 5 Hz, quaternary C), 155.0 (d, $^2J_{CH}$ 5 Hz, quaternary C), 159.0 (q, $^2J_{CH}$ 7 Hz, 1-C), and 162.9 (d, $^2J_{CH}$ 4 Hz, quaternary C); *m/z* 199 (M^+, 100%), 184(58), 171(46), 143(15), 128(23), 115(12), and 101(12).

t-Butyl 3-*Oxopyrano*[4,3-b]*indole*-5-*carboxylate* (**8a**).—To a cooled suspension (0 °C) of sodium hydride (12.9 mg, 0.32 mmol) in dimethylformamide (6 ml), was added dropwise a solution of pyrano[4,3-*b*]indol-3-one (**7a**) (54 mg, 0.29 mmol) in dimethylformamide (10 ml). After addition was complete, the mixture was stirred, under nitrogen, at room temperature for 0.5 h. The mixture was recooled to 0 °C and di-t-butyl oxydiformate (326 mg, 1.47 mmol) in dimethylformamide (10 ml) was added. The mixture was allowed to warm to room temperature and stirred for a further 2.5 h. Water (150 ml) was added and the solution extracted with ethyl acetate (3 × 50 ml). The organic extracts were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography (ether) to give the *title compound* (**8a**) (83.2 mg, 100%) as a beige solid, m.p. 131 °C (decomp.) (Found: C, 67.6; H, 5.6; N, 4.7. $C_{16}H_{15}NO_4$ requires C, 67.4; H, 5.3; N, 4.9%); ν_{max}(Nujol) 1 736 (urethane C=O), 1 708 (pyrone C=O), 1 666, 1 575, 1 410, 1 335, 1 311, 1 240, 1 199, 1 153, and 1 124 cm^{-1}; λ_{max}(tetrahydrofuran) 256 (ε 29 464), 265 (32 768), 297 (5 268), and 309 nm (4 821); δ_H[270 MHz; $(CD_3)_2CO$] 1.73 (9 H, s, t-Bu), 6.65 (1 H, d, *J* 1 Hz, 4-H), 7.31 (1 H, td, *J* 7, 7, and 1 Hz), 7.46 (1 H, td, *J* 7, 7 and 1 Hz), 7.86 (1 H, d, *J* 7 Hz), 8.07 (1 H, d, *J* 7 Hz), and 8.52 (1 H, d, *J* 1 Hz); *m/z* 285 (M^+, 9%), 229(22), 185(57), 157(10), 129(12), and 57(100).

t-Butyl 1-*Methyl*-3-*oxopyrano*[4,3-b]*indole*-5-*carboxylate* (**8b**).—To a cooled suspension (0 °C) of sodium hydride (32 mg, 0.80 mmol) in dimethylformamide (10 ml), was added dropwise a solution of 1-methylpyrano[4,3-*b*]indol-3-one (**8a**) (131 mg, 0.66 mmol) in dimethylformamide (10 ml). After addition was complete, the mixture was stirred, under nitrogen, at room temperature for 0.5 h. The mixture was recooled to 0 °C and di-t-butyl oxydiformate (720 mg, 3.30 mmol) in dimethylformamide (15 ml) was added. The mixture was allowed to warm to room temperature and then stirred for a further 2.5 h. Water (150 ml) was added and the solution extracted with ethyl acetate (3 × 50 ml). The organic extracts were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography (ether) to give the *title compound* (**8b**) (173 mg, 88%) as a beige solid, m.p. 151 °C (decomp.) (Found: C, 68.0; H, 5.7; N, 4.5. $C_{17}H_{17}NO_4$ requires C, 68.2; H, 5.7; N, 4.7%); ν_{max}(Nujol) 1 737 (urethane C=O), 1 704 (pyrone C=O), 1 597, 1 577, 1 296, and 1 160 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.72 (9 H, s, t-Bu), 2.70 (3 H, s, Me), 6.57 (1 H, s, 4-H), 7.34 (1 H, td, *J* 7, 7, and 1 Hz), 7.45 (1 H, dt, *J* 8, 8, and 1 Hz), 7.82 (1 H, d, *J* 7 Hz), and 8.12 (1 H, d, *J* 8 Hz); *m/z* 299 (M^+, 4%), 243(17), 199(100), 184(47), 171(38), 128(18), and 57(37).

Dimethyl 9H-*Carbazole*-2,3-*dicarboxylate* (**9a**).—A mixture of pyrano[4,3-*b*]indol-3-one (**7a**) (20.4 mg, 0.11 mmol) and dimethyl acetylenedicarboxylate (50 μl, 0.41 mmol) in chlorobenzene was refluxed under nitrogen for 44 h. The solvent was evaporated and the residue chromatographed (ether) to give the title carbazole (**9a**) (28.6 mg, 92%) as a crystalline compound, m.p. 145.5–146.5 °C (lit.,[13] 136–137 °C) (Found: C, 67.9; H, 4.6; N, 4.9. Calc. for $C_{16}H_{13}NO_4$: C, 67.8; H, 4.6; N, 4.9%); ν_{max}($CHCl_3$) 3 465 (NH), 1 718 (C=O), 1 436, 1 348, 1 267, 1 111, and 1 070 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 3.87 (6 H, s, 2 × OMe), 7.28 (1 H, t, *J* 7 Hz), 7.50 (1 H, t, *J* 7 Hz), 7.61 (1 H, d, *J* 8 Hz), 7.80 (1 H, s, 1-H), 8.26 (1 H, d, *J* 8 Hz), 8.59 (1 H, s, 4-H), and 10.85 (1 H, br, NH); *m/z* 283 (M^+, 81%) and 252(100).

9-*t-Butyl* 2,3-*Dimethyl* 9H-*Carbazole*-2,3,9-*tricarboxylate* (**9b**).—A mixture of t-butyl 3-oxopyrano[4,3-*b*]indole-5-carboxylate (**8a**) (47.6 mg, 0.17 mmol) and dimethyl acetylenedicarboxylate (72 μl, 0.59 mmol) in chlorobenzene was refluxed under nitrogen for 20 h. The solvent was evaporated and the residue chromatographed (ether) to give a mixture of NH and NBoc carbazoles (**9a**) and (**9b**). This mixture was heated neat for 2 h at 180 °C and then rechromatographed (ether) to give the NH carbazole (**9a**) (38.5 mg, 82%) as a crystalline compound.

Dimethyl 4-*Methyl*-9H-*carbazole*-2,3-*dicarboxylate* (**9c**).—A mixture of 1-methylpyrano[4,3-*b*]indol-3-one (**7b**) (17.2 mg, 0.09 mmol) and dimethyl acetylenedicarboxylate (25 μl, 0.20 mmol) in chlorobenzene was refluxed under nitrogen for 144 h. The solvent was evaporated and the residue chromatographed (ether) to give the *title carbazole* (**9c**) (7.7 mg, 30%) as a crystalline compound, m.p. 130–131 °C (Found: C, 68.7; H, 5.0; N, 4.7. $C_{17}H_{15}NO_4$ requires C, 68.7; H, 5.1; N, 4.7%); ν_{max}($CHCl_3$) 3 468 (NH), 1 719 (C=O), 1 438, 1 342, 1 259, and 1 077 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 2.85 (3 H, s, Me), 3.88 (6 H, s, 2 × OMe), 7.28 (1 H, t, *J* 8 Hz), 7.51 (1 H, t, *J* 8 Hz), 7.63 (1 H, d, *J* 8 Hz), 8.01 (1 H, s, 1-H), 8.29 (1 H, d, *J* 8 Hz), and 10.81 (1 H, br, NH); *m/z* 297 (M^+, 100%), 266(99), 265(73), 250(19), 207(62), and 179(31).

Ethyl 9H-*Carbazole*-2-*carboxylate* (**9d**) and *Ethyl* 9H-*Carbazole*-3-*carboxylate* (**10d**).—A mixture of pyrano[4,3-*b*]indol-3-one (**7a**) (36.7 mg, 0.20 mmol) and ethyl propiolate (0.40 ml, 3.9 mmol) in chlorobenzene was refluxed under nitrogen for 167 h. The solvent was evaporated and the residue chromatographed (dichloromethane) to give the title carbazoles (**9d**):(**10d**) in a 1:1.2 ratio (42.8 mg, 90%); ν_{max}($CHCl_3$) 3 471 (NH), 1 704 (C=O), 1 254, and 1 097 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.33–1.40 (m, ethoxy CH_3, both isomers), 4.38 (q, *J* 7 Hz, OCH_2, both isomers), 7.19–7.30 (m, both isomers), 7.40–7.50 (m, both isomers), 7.53–7.60 (m, both isomers), 7.87 (dd, *J* 8.3 and 1.5 Hz, minor isomer), 8.08 (dd, *J* 8.3 and 2 Hz, major isomer), 8.15–8.25 (m, both isomers), 8.82 (d, *J* 2 Hz, major isomer, 4-H), 10.60 (br, minor isomer, NH), and 10.71

(br, major isomer, NH); *m/z* 239 (M^+, 100%), 194(65), and 166(27).

9-t-Butyl 2-Ethyl 9H-*Carbazole*-2,9-*dicarboxylate* (**9e**) *and* 9-*t-Butyl 3-Ethyl* 9*H*-*Carbazole*-3,9-*dicarboxylate* (**10e**).—A mixture of t-butyl 3-oxopyrano[4,3-*b*]indole-5-carboxylate (**8a**) (29.5 mg, 0.10 mmol) and ethyl propiolate (0.21 ml, 2.1 mmol) in chlorobenzene was refluxed under nitrogen for 25 h. The solvent was evaporated and the residue chromatographed (dichloromethane and methanol) to give pyrano[4,3-*b*]indol-3-one (**7a**) (6.7 mg, 35%); a mixture of ethyl 9*H*-carbazole-2-carboxylate (**9d**) and ethyl 9*H*-carbazole-3-carboxylate (**10d**) in a 1:1 ratio (12.8 mg, 52%) and the *title carbazoles* (**9e**):(**10e**) in a 1.5:1 ratio (3.5 mg, 10%); ν_{max}($CHCl_3$) 1 713 (C=O), 1 371, 1 330, 1 245, and 1 156 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.39–1.44 (m, ethoxy CH_3, both isomers), 1.79 (9 H, s, minor isomer, t-Bu), 1.81 (9 H, s, major isomer, t-Bu), 4.40 (q, *J* 7 Hz, OCH_2, both isomers), 7.41–7.47 (m, both isomers), 7.53–7.63 (m, both isomers), 8.05 (1 H, dd, *J* 8 and 1 Hz, major isomer), 8.15–8.43 (m, both isomers), 8.75 (1 H, d, *J* 1 Hz, minor isomer), and 9.05 (1 H, d, *J* 1 Hz, major isomer); *m/z* 339 (M^+, 22%), 283(52), 239(70), and 57(100). This mixture of NBoc carbazoles was heated neat for 6 h at 140 °C to give the corresponding NH carbazoles (**9d**):(**10d**) in a 1.5:1 ratio.

Ethyl 4-*Methyl*-9H-*carbazole*-2-*carboxylate* (**9f**) and *Ethyl* 4-*Methyl*-9H-*carbazole*-3-carboxylate (**10f**).—A mixture of 1-methylpyrano[4,3-*b*]indol-3-one (**7b**) (30.2 mg, 0.15 mmol) and ethyl propiolate (0.31 ml, 3.1 mmol) in chlorobenzene was refluxed under nitrogen for 425 h. The solvent was evaporated and the residue chromatographed (dichloromethane + 10% ethyl acetate) to give the *title carbazoles* (**9f**):(**10f**) in a 1:2 ratio (30.0 mg, 78%) (Found: C, 75.8; H, 6.0; N, 5.4. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); ν_{max}($CHCl_3$) 3 470 (NH), 1 703 (C=O), 1 602, 1 331, 1 250, and 1 073 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.39 (t, *J* 7 Hz, ethoxy CH_3, both isomers), 2.90 (s, minor isomer, Me), 3.16 (s, major isomer, Me), 4.35 (m, OCH_2, both isomers), 7.22–7.29 (m, both isomers), 7.39–7.50 (m, both isomers), 7.56–7.63 (m, both isomers), 7.66 (s, minor isomer), 7.96 (d, *J* 8 Hz, major isomer), 8.06 (s, minor isomer), 8.23 (d, *J* 8 Hz, minor isomer), 8.30 (d, *J* 8 Hz, major isomer), 10.60 (br, minor isomer, NH), and 10.70 (br, major isomer, NH); *m/z* 253 (M^+, 100%), 225(14), 208(52), 180(31), and 104(12).

Methyl 2-*Phenyl*-9H-*carbazole*-3-*carboxylate* (**10g**).—A mixture of pyrano[4,3-*b*]indol-3-one (**7a**) (40.7 mg, 0.22 mmol) and methyl phenylpropiolate (87.5 mg, 0.55 mmol) in bromobenzene was heated (140 °C) under nitrogen for 241 h. The solvent was evaporated and the residue chromatographed (dichloromethane + 5% light petroleum) to give the *title carbazole* (**10g**) (18.4 mg, 28%) as a crystalline compound, m.p. 165–166 °C (Found: C, 79.5; H, 4.9; N, 4.5. $C_{20}H_{15}NO_2$ requires C, 79.7; H, 5.0; N, 4.65%); ν_{max}($CHCl_3$) 3 468 (NH), 1 712 (C=O), 1 633, 1 610, 1 494, 1 467, 1 434, 1 347, 1 259, 1 243, and 1 093 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 3.61 (3 H, s, OMe), 7.2–7.6 (9 H, m), 8.24 (1 H, d, *J* 8 Hz), 8.64 (1 H, s, 4-H), and 10.70 (1 H, br, NH); *m/z* 301 (M^+, 100%), 270(68), 241(26), and 121(19).

Reaction of t-Butyl 3-*Oxopyrano*[4,3-b]*indole*-5-*carboxylate* (**8a**) *with Methyl Phenylpropiolate*.—A mixture of t-butyl 3-oxopyrano[4,3-*b*]indole-5-carboxylate (**8a**) (28 mg, 0.10 mmol) and methyl phenylpropiolate (31.4 mg, 0.20 mmol) in chlorobenzene was refluxed under nitrogen for 48 h. The solvent was evaporated and the residue chromatographed (dichloromethane + 5% methanol) to give methyl 2-phenyl-9*H*-carbazole-3-carboxylate (**10g**) (11.8 mg, 40%) and pyrano[4,3-*b*]indol-3-one (**7a**) (10.9 mg, 60%).

Ethyl 2-*Trimethylsilyl*-9H-*carbazole*-3-*carboxylate* (**10i**).—A mixture of pyrano[4,3-*b*]indol-3-one (**7a**) (30.5 mg, 0.16 mmol) and ethyl 3-trimethylsilylpropynoate (82.9 mg, 0.49 mmol) in chlorobenzene was refluxed under nitrogen for 262 h. The solvent was evaporated and the residue chromatographed (dichloromethane) to give the *title carbazole* (**10i**) (12.5 mg, 24%) as a crystalline compound, m.p. 120.5–123 °C (Found: M^+, 311.1 340. $C_{18}H_{21}NO_2Si$ requires *M*, 311.1 342); ν_{max}($CHCl_3$) 3 469 (NH), 1 704 (C=O), 1 605, 1 467, 1 371, 1 335, 1 245, 1 104, and 844 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 0.36 (9 H, s, $SiMe_3$), 1.42 (3 H, t, *J* 7 Hz, ethoxy CH_3), 4.40 (2 H, q, *J* 7 Hz, ethoxy CH_2), 7.25 (1 H, t, *J* 8 Hz), 7.45 (1 H, t, *J* 8 Hz), 7.58 (1 H, d, *J* 8 Hz, 8-H), 7.86 (1 H, s, 1-H), 8.21 (1 H, d, *J* 8 Hz, 5-H), 8.88 (1 H, s, 4-H), and 10.65 (1 H, br, NH); *m/z* 311 (M^+, 19%), 296(100), and 268(76).

Ethyl 9H-*Carbazole*-3-*carboxylate* (**10d**).—Ethyl 2-trimethylsilyl-9-*H*-carbazole-3-carboxylate (**10i**) (9.7 mg, 0.03 mmol) was dissolved in trifluoroacetic acid–water (2:1) (3 ml) and heated at 70 °C for 2 h. The reaction mixture was then cooled to room temperature and allowed to stand for 14 h. The mixture was diluted with water (30 ml) and extracted with ether (3 × 20 ml). The ethereal extracts were washed with saturated aqueous sodium hydrogen carbonate until the washings remained basic, then with water, followed by brine, after which it was dried ($MgSO_4$). The solution was concentrated under reduced pressure to give the title compound (**10d**) (6.1 mg, 82%), m.p. 165–168 °C (lit.,[14] 165–167 °C); ν_{max}($CHCl_3$) 3 470 (NH), 1 703 (C=O), 1 252, and 1 098 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.40 (3 H, t, *J* 7 Hz, ethoxy CH_3), 4.38 (2 H, q, *J* 7 Hz, OCH_2), 7.26 (1 H, td, *J* 8, 8, and 1 Hz), 7.45 (1 H, td, *J* 8, 8 and 1 Hz), 7.57 (1 H, dd, *J* 8, and 1 Hz), 8.08 (1 H, dd, *J* 8 and 2 Hz), 8.23 (1 H, dd, *J* 8 and 2 Hz), 8.82 (1 H, s, 4-H), and 10.73 (1 H, br, NH); *m/z* 239 (M^+, 100%), 194(91), and 166(31).

Reaction of Pyrano[4,3-b]*indol*-3-*one* (**7a**) *with Methyl Tetrolate*.—A mixture of pyrano[4,3-*b*]indol-3-one (**7a**) (60 mg, 0.32 mmol) and methyl tetrolate (0.13 ml, 1.3 mmol) in chlorobenzene was refluxed under nitrogen for 528 h. No carbazole products were detected by TLC and so the reaction was abandoned.

Reaction of 1-*Methylpyrano*[4,3-b]*indol*-3-*one* (**7b**) *with Ethyl* 3-*trimethylsilylpropynoate*.—A mixture of 1-methylpyrano[4,3-*b*]indol-3-one (**7b**) (27.7 mg, 0.14 mmol) and ethyl 3-trimethylsilylpropynoate (41.3 mg, 0.24 mmol) in chlorobenzene was refluxed under nitrogen for 1 344 h. No carbazole products were detected by TLC and so the reaction was abandoned.

Reaction of t-Butyl 1-*Methyl*-3-*oxopyrano*[4,3-b]*indole*-5-*carboxylate* (**8b**) *with Ethyl* 3-*Trimethylsilylpropynoate*.—A mixture of t-butyl 1-methyl-3-oxopyrano[4,3-*b*]indole-5-carboxylate (**8b**) (14.2 mg, 0.05 mmol) and ethyl 3-trimethylsilylpropynoate (16 mg, 0.09 mmol) in chlorobenzene was refluxed under nitrogen for 96 h. The solvent was evaporated and the residue chromatographed (ether + 5% methanol) to give 1-methylpyrano[4,3-*b*]indol-3-one (**7b**) (8.1 mg, 86%). No carbazole products were isolated.

Acknowledgements

We thank Glaxo Group Research, Greenford, for a studentship (to K. F. R.), the Royal Society of Chemistry for a Hickinbottom

fellowship (to C. J. M.), Drs. B. C. Ross and B. Porter for helpful discussions, Mr. R. N. Sheppard for invaluable advice on the NMR spectroscopy, and Lonza Ltd. for a generous gift of Meldrum's acid.

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Paper 9/03159F
Received 26th *July* 1989
Accepted 8th *September* 1989