Diels-Alder Reactivity of Pyrano[3,4-*b*]indol-3-ones. Part 3.[1] Intramolecular Diels-Alder Reactions

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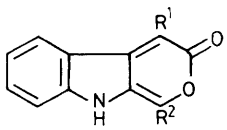
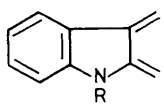
Heating the 1-alkynylpyrano[3,4-*b*]indol-3-ones (**5**), prepared from the alkynoic acids (**3**), results in intramolecular Diels–Alder reaction involving the indole-2,3-quinodimethane diene with subsequent extrusion of carbon dioxide to give the cycloalka[*a*]carbazoles (**6**). The pyranoindolones need not be isolated, since the 2-acylindol-3-ylacetic acids (**8**) undergo cyclodehydration and intramolecular Diels–Alder reaction when heated in an acid anhydride as solvent. In contrast to the intramolecular Diels–Alder reaction involving the acetylenic compound (**5a**), the olefin (**9**) was a much poorer substrate.

We have recently described the use of pyrano[3,4-*b*]indol-3-ones (**1**) as stable, isolable indole-2,3-quinodimethanes, and their intermolecular Diels–Alder reactions with alkynes to give substituted carbazoles.[1,2] In contrast, the indole-2,3-quinodimethanes (**2**) are highly reactive intermediates which often give poor yields of Diels–Alder adducts when generated *in situ* in the presence of a dienophile,[3] although the intramolecular Diels–Alder reaction of such non-isolable indole-2,3-quinodimethanes is a useful reaction that has been exploited in synthesis.† We now report in detail our results on the first examples of the intramolecular Diels–Alder reaction involving the pyranoindolone diene system.[4]



(**1**)

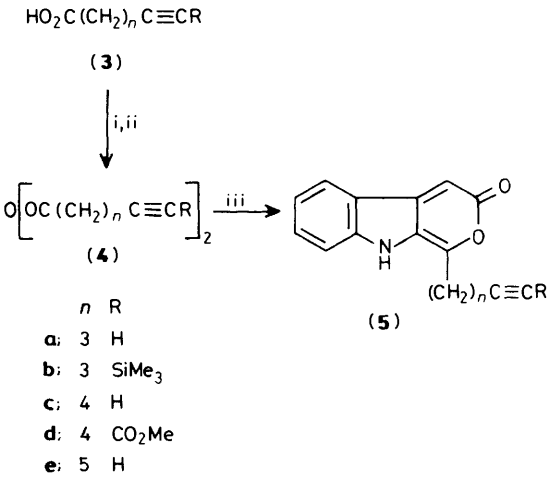


(**2**)

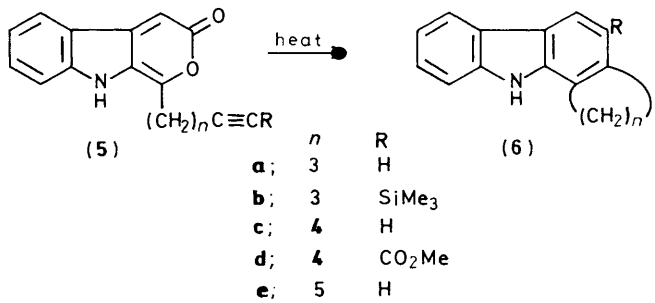
Results and Discussion

The substrates for the intramolecular Diels–Alder reaction are 1-substituted pyrano[3,4-*b*]indol-3-ones (**5**) bearing an alkyl chain with a terminal triple bond. These were prepared from the corresponding alkynoic acids (**3**) by conversion into the anhydride (**4**), followed by reaction with indol-3-ylacetic acid in the presence of boron trifluoride–diethyl ether (Scheme 1).[1,2] The alkynoic acids (**3**) were prepared using standard chemistry, the details of which are given in the Experimental section.

On heating in refluxing bromobenzene for 3 h, the pentynylpyranoindolone (**5a**) underwent intramolecular Diels–Alder reaction, followed by extrusion of carbon dioxide to give the dihydrocyclopenta[*a*]carbazole (**6a**) (79%) (Scheme 2). The good yield of this intramolecular Diels–Alder reaction involving an unactivated triple bond as the 2π-component is in direct contrast to the *inter*molecular reactions of such alkynes which proceed in poor yield. For example, hept-1-yne reacts with 1-methylpyrano[3,4-*b*]indol-3-one to give 1-methyl-3-pentylcarbazole in only 16% yield after heating for 72 h in boiling bromobenzene.[1] The *intra*molecular variant also proceeds at lower temperatures than the intermolecular reaction, and



Scheme 1. *Reagents:* i, NaH, THF; ii, $(COCl)_2$, benzene, heat; iii, indol-3-ylacetic acid, BF_3–Et_2O



Scheme 2.

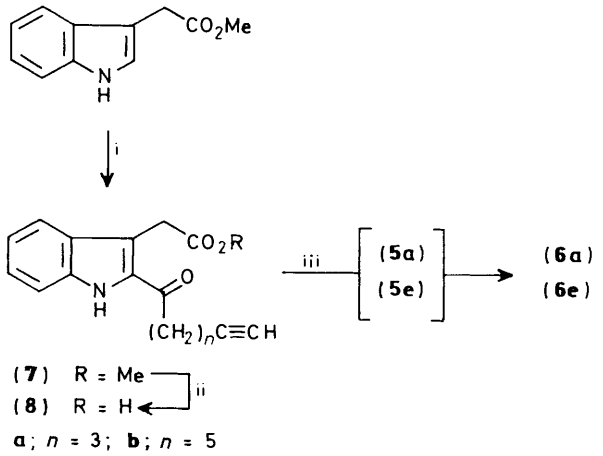
heating the precursor (**5a**) for 48 h in boiling tetrahydrofuran (THF) or for 20 h in boiling toluene gives the carbazole (**6a**) in 58 and 73% yield respectively.

The pyranoindolone (**5b**) bearing the bulky trimethylsilyl group also undergoes facile intramolecular Diels–Alder reaction, as do the hexynylpyranoindolones (**5c**) and (**5d**), to give the silylated cyclopentacarbazole (**6b**) (82%), the known[5] tetrahydrobenzo[*a*]carbazole (**6c**) (53%), and the corresponding ester (**6d**) (63%). The heptynylpyranoindolone (**5e**), however, required heating at 190 °C in benzonitrile to effect the intramolecular Diels–Alder reaction, which only then gave the tetrahydrocycloheptacarbazole (**6e**) in 35% yield. The form-

† For recent examples of this reaction see K. Cardwell, B. Hewitt, and P. Magnus, *Tetrahedron Lett.*, 1987, **28**, 3303; P. Magnus, M. Ladlow, and P. M. Cairns, *ibid.*, p. 3307; M. Herslof and A. R. Martin, *ibid.*, p. 3423 and references therein.

ation of 7-membered rings by intramolecular Diels–Alder reactions is generally less favourable than the corresponding reactions which form 5- or 6-membered rings.[6]

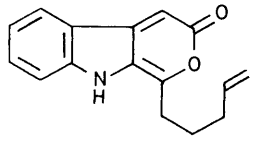
In order to carry out the intramolecular Diels–Alder reaction, the pyranoindolones need not be isolated. In this variant of the reaction, the precursors are simple 2-acylindol-3-ylacetic acids (**8**), which are prepared by acylation of methyl indol-3-ylacetate in the presence of zinc chloride, followed by hydrolysis of the ester (**7**) (Scheme 3). Heating the acylindol-3-ylacetic acid (**8a**)



Scheme 3. *Reagents:* i, $HC{\equiv}C(CH_2)_nCOCl$, $ZnCl_2$, CH_2Cl_2; ii, KOH, aq. MeOH–THF; iii, acetic (or butyric) anhydride, heat

in refluxing acetic anhydride for 3 h gives the carbazole (**6a**) directly in 56% yield, presumably *via* initial cyclodehydration to the pyrone (**5a**), followed by intramolecular Diels–Alder reaction as before. Similarly, the indole (**8b**) gives the cycloheptacarbazole (**6e**) on heating in butyric anhydride.

Finally we attempted to effect an intramolecular Diels–Alder reaction of an olefinic substrate. However, this was less satisfactory, and heating the 1-(pent-4-enyl)pyranoindolone (**9**), prepared from hex-5-enoic acid[7] in the usual way, in bromobenzene gave the dihydrocyclopentacarbazole (**6a**) in only 16% yield. The reaction presumably proceeds *via* the corresponding 1,4-dihydrocarbazole which is dehydrogenated under the reaction conditions; when the reaction was carried out in the presence of palladium–charcoal as dehydrogenating agent, the yield of the aromatic carbazole (**6a**) was increased to 43%.



(**9**)

Experimental

270 MHz ^{1}H N.m.r. spectra were recorded on a JEOL GSX270 instrument. For other general points, see ref. 1.

Hex-5-ynoic Acid (**3a**).—Jones reagent was added to a stirred solution of hex-5-yn-1-ol (5.00 g, 51 mmol) in acetone (50 ml), with external cooling until the orange colour of the oxidant persisted. After the addition was complete, the reaction was stirred at room temperature for 30 min, and then diluted with water (100 ml). The aqueous mixture was extracted with ether and the combined ethereal extracts back extracted with aqueous sodium hydroxide (1M; 2 × 70 ml). The combined sodium hydroxide extracts were acidified with concentrated hydrochloric acid, and extracted with ether. The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure to give a pale yellow liquid, which was distilled under reduced pressure to give the title compound (**3a**) (3.85 g, 67%), b.p. 76—78 °C at 0.3 mmHg (lit.,[8] b.p. 122—124 °C at 20 mmHg), $\nu_{max.}$(film) 3 500—2 400, 3 300, 2 120, and 1 710 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.76—1.88 (2 H, m), 1.97 (1 H, t, *J* 2.5 Hz), 2.25 (2 H, dt, *J* 6.6 Hz and 2.5 Hz), 2.48 (2 H, t, *J* 7.3 Hz), and 11.45 (1 H, br); *m/z* 111[(M^+ − H), 4%], 95(4), and 70(100).

Hex-5-ynoic Anhydride (**4a**).—Hex-5-ynoic acid (**3a**) (3.77 g, 33.67 mmol) in THF (10 ml) was added to a stirred suspension of sodium hydride (929 mg, 38.71 mmol) in THF (50 ml), over 10 min with external cooling. The reaction was allowed to stir at room temperature for 1 h, then the solvent was evaporated off under reduced pressure, and the dry salt suspended in benzene (40 ml). Oxalyl chloride (1.54 ml, 17.67 mmol) was added and the reaction mixture was refluxed under nitrogen for 2 h. After being cooled to room temperature, the reaction mixture was filtered through a pad of Celite, the filtrate concentrated under reduced pressure, and the residue distilled under reduced pressure to give the title compound (**4a**) (1.78 g, 51%), b.p. 122—124 °C at 0.6 mmHg, $\nu_{max.}$(film) 3 300, 2 120, 1 815, 1 700, and 1 050br cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.79—1.91 (4 H, m), 1.97 (2 H, t, *J* 2.5 Hz), 2.28 (4 H, dt, *J* 6.8 and 2.5 Hz), and 2.59 (4 H, t, *J* 7.3 Hz).

1-(*Pent-4-ynyl*)*pyrano*[3,4-b]*indol-3-one* (**5a**).—Freshly distilled boron trifluoride–diethyl ether (1 ml) was added dropwise over 20 min to a stirred solution of indol-3-ylacetic acid (1.05 g, 6.01 mmol) and hex-5-ynoic anhydride (**4a**) (1.65 g, 8.01 mmol) in ether (3 ml) at room temperature. The reaction was allowed to stir for a further 40 min. Ether (15 ml) was added and the orange solid filtered off, washed with more ether (50 ml), triturated with aqueous sodium hydrogen carbonate (half saturated; 4 × 50 ml), and washed with water (4 × 50 ml). The solid was sucked dry on the sinter and washed with more ether (10 ml). After being dried *in vacuo* overnight, the solid was chromatographed on silica (ether–methanol) to give the *title compound* (**5a**) as a bright yellow-orange solid (375 mg, 25%), m.p. 139—143 °C (Found: C, 76.3; H, 5.2; N, 5.7. $C_{16}H_{13}NO_2$ requires C, 76.5; H, 5.2; N, 5.6%); $\nu_{max.}$(Nujol) 3 330, 3 150br, 1 690, 1 612, 1 560, and 667 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 1.81—1.93 (2 H, m), 2.25 (2 H, dt, *J* 7 and 2.5 Hz), 2.83 (1 H, t, *J* 2.5 Hz), 2.88 (2 H, t, *J* 7.6 Hz), 6.57 (1 H, s), 7.00 (1 H ~t, *J* 7.8 Hz), 7.20 (1 H, d, *J* 7.8 Hz), 7.50 (1 H, ~t, *J* 7.8 Hz), 7.97 (1 H, d, *J* 7.8 Hz), and 10.45 (1 H, br, NH); *m/z* 251 (M^+, 1%), 207 (100), and 44 (28).

2,3-*Dihydro*-1H,10H-*cyclopenta*[a]*carbazole* (**6a**).—(*a*) A solution of the pyranoindolone (**5a**) (40.5 mg, 0.16 mmol) in bromobenzene (8 ml) was heated under reflux under nitrogen for 3 h. The solvent was evaporated off and the residue chromatographed to give the *title compound* (**6a**) (26.3 mg, 79%), m.p. 154—156 °C (Found: C, 86.8; H, 6.3; N, 6.8. $C_{15}H_{13}N$ requires C, 86.9; H, 6.3; N, 6.8%); $\nu_{max.}$(Nujol) 3 420, 810, 745, and 730 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 2.21—2.33 (2 H, m), 3.08—3.16 (4 H, m), 7.17 (1 H, d, *J* 7.6 Hz), 7.23 (1 H, ddd, *J* 7.5, 7.5, and 1.5 Hz), 7.36—7.46 (2 H, m), 7.88 (1 H, br, NH), 7.91 (1 H, d, *J* 7.6 Hz), and 8.06 (1 H, d, *J* 7.5 Hz); *m/z* 207 (M^+, 100%).

(*b*) A solution of the pyranoindolone (**5a**) (20 mg, 0.08 mmol) in THF (8 ml) was heated under reflux under nitrogen for 48 h. The solvent was evaporated and the residue chromatographed to give the title compound (**6a**) (9.5 mg, 58%) with identical ^{1}H n.m.r. and t.l.c. properties to the previous sample described above.

(*c*) A solution of the pyranoindolone (**5a**) (18 mg, 0.07 mmol) in toluene (10 ml) was heated under reflux under nitrogen for 20 h. The solvent was evaporated and the residue chromatographed to give the title compound (**6a**) (10.9 mg, 73%) with identical ^{1}H n.m.r. and t.l.c. properties to the previous sample described above.

6-*Trimethylsilylhex*-5-*ynoic Acid* (**3b**).—A solution of 1-iodo-5-trimethylsilylpent-4-yne[9] (5.91 g, 22.22 mmol) in dry ether (10 ml) was added to a suspension of magnesium turnings (640 mg, 26.67 mmol) in ether (60 ml). After 40 min the Grignard had formed and the contents of the flask were poured onto solid carbon dioxide (~50 g). After all the carbon dioxide had evaporated, dilute hydrochloric acid (0.5M; 100 ml) was added and the resulting mixture was extracted with ether. The combined ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow oil, which was chromatographed (ether–light petroleum) to give the title compound (**3b**) (1.45 g, 35%) as a pale yellow oil, $\nu_{max.}$(film) 3 500—2 460br, 1 710, 1 410, 1 250, 1 050, 840, and 760 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.12 (9 H, s), 1.75—1.86 (2 H, m), 2.28 (2 H, t, *J* 6.3 Hz), 2.46 (2 H, t, *J* 7 Hz), and 11.08 (1 H, br, CO_2H).

Bis(6-*trimethylsilylhex*-5-*ynoic*) *Anhydride* (**4b**).—This was prepared as described for (**4a**) in 90% yield. The anhydride was sufficiently pure for subsequent reactions without distillation, $\nu_{max.}$(film) 2 176, 1 821, 1 752, 1 251, 1 038, 844, and 761 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 0.14 (18 H, s), 1.81—1.91 (4 H, m), 2.32 (4 H, t, *J* 6.7 Hz), and 2.59 (4 H, t, *J* 7 Hz).

1-(5-*Trimethylsilylpent*-4-*ynyl*)*pyrano*[3,4-b]*indol*-3-*one* (**5b**).—Addition of freshly distilled boron trifluoride–diethyl ether (0.5 ml) to a stirred solution of indol-3-ylacetic acid (400 mg, 2.29 mmol) and bis(6-trimethylsilylhex-5-ynoic) anhydride (**4b**) (930 mg, 2.66 mmol) in ether (1 ml) at 0 °C as described for (**5a**) followed by a similar work-up and chromatography gave the *title compound* (**5b**) as a bright yellow solid (91 mg, 12%), m.p. 155—158 °C (Found: M^+, 323.1336. $C_{19}H_{21}NO_2Si$ reauires *M*, 323.1342); $\nu_{max.}$(Nujol) 3 173, 2 178, 1 696, 1 630, 1 614, 1 568, 1 323, 1 226, and 842 cm^{-1} δ_H[270 MHz; $(CD_3)_2SO$] 0.05 (9 H, s), 1.82—1.93 (2 H, m), 2.32 (2 H, t, *J* 7.2 Hz), 2.87 (2 H, t, *J* 7.2 Hz), 6.55 (1 H, s), 7.00 (1 H, ~t, *J* 7.7 Hz), 7.20 (1 H, d, *J* 7.7 Hz), 7.50 (1 H, ~t, *J* 7.7 Hz), 7.96 (1 H, d, *J* 7.7 Hz), and 10.38 (1 H, br, NH); *m/z* 323 (M^+, 1%), 308 (1), 279 (70), and 264 (100%).

2,3-*Dihydro*-3-*trimethylsilyl*-1H,10H-*cyclopenta*[a]*carbazole* (**6b**).—A solution of the pyranoindolone (**5b**) (52 mg, 0.16 mmol) in bromobenzene (25 ml) was heated under reflux under nitrogen for 1.15 h. The mixture was evaporated and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**6b**) (37 mg, 82%), m.p. 84—88 °C (Found: M^+, 279.1442. $C_{18}H_{21}NSi$ requires *M*, 279.1443); $\nu_{max.}$(CCl_4) 3 479, 1 612, 1 467, 1 323, 1 249, 1 233, 1 127, and 935 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.4 (9 H, s), 2.22—2.34 (2 H, m), 3.09 (2 H, t, *J* 7.1 Hz), 3.19 (2 H, t, *J* 7.1 Hz), 7.24 (1 H ~t, *J* 7.8 Hz), 7.35—7.45 (2 H, m), 7.88 (1 H, br, NH), 8.08 (1 H, s), and 8.08 (1 H, d, *J* 7.8 Hz).

Hept-6-*ynoic Acid* (**3c**).—5-Bromo-1-t-butyldimethylsiloxypentane (18.32 g, 65.2 mmol) in DMF (60 ml) was added to a stirred suspension of sodium acetylide (6.2 g, 129.2 mmol) in dry DMF* (70 ml) at 0 °C over 10 min. The reaction was stirred at room temperature for 16 h, and then carefully poured into an ice–water mixture (200 g). The aqueous mixture was extracted with ether and the combined ethereal extracts washed with water and brine, dried ($MgSO_4$), and the solvent evaporated off under reduced pressure to give 1-t-butyldimethylsiloxyhept-6-yne (13.83 g), $\nu_{max.}$(film) 3 320, 1 260, 1 100, 840, and 780 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.1 (6 H, s), 0.85 (9 H, s), 1.30—1.68 (6 H, m), 1.85 (1 H, t, *J* ~2 Hz), 1.98—2.32 (2 H, m), and 3.58 (2 H, ~t, *J* 6.4 Hz).

The above crude product was treated with acetic acid–THF–water (3:1:1; 100 ml), and the mixture heated at 80—90 °C for 1.5 h. The reaction mixture was then poured into aqueous sodium hydroxide (2M; 200 ml), and the aqueous mixture was extracted with ether. The combined ethereal extracts were washed with water and brine, dried ($MgSO_4$), and the solvent evaporated off under reduced pressure to give a pale yellow liquid which consisted of the alcohol and silyl derivatives. This crude mixture was subjected to Jones oxidation exactly as described for (**3a**) to give the title compound (**3c**) as a colourless liquid (4.3 g, 52%), b.p. 70—72 °C at 0.2 mmHg (lit.,[8] b.p. 78—80 °C at 0.04 mmHg, lit.,[10] b.p. 93—94 °C at 1 mmHg), $\nu_{max.}$(film) 3 500—2 400, 3 300, 2 120, and 1 705 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.50—1.64 (2 H, m), 1.66—1.80 (2 H, m), 1.94 (1 H, t, *J* 2.5 Hz), 2.20 (2 H, dt, *J* 7.0 and 2.5 Hz), 2.37 (2 H, t, *J* 7.3 Hz), and 10.80 (1 H, br); *m/z* 125 (M^+ − H, 1%), 84 (36), and 81 (100).

Hept-6-*ynoic Anhydride* (**4c**).—Prepared as described for compound (**4a**) in 95% yield. The anhydride was sufficiently pure for subsequent reactions without distillation, $\nu_{max.}$(film) 3 300, 2 120, 1 820, 1 750, and 1 050br cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.44—1.89 (8 H, m), 1.95 (2 H, t, *J* ~2 Hz), 2.22 (4 H, dt, *J* 6, and ~2 Hz), and 2.48 (4 H, t, *J* 7 Hz).

1-(*Hex*-5-*ynyl*)*pyrano*[3,4-b]*indol*-3-*one* (**5c**).—Addition of freshly distilled boron trifluoride–diethyl ether (1 ml) to a stirred solution of indol-3-ylacetic acid (920 mg, 5.26 mmol) and hept-6-ynoic anhydride (**4c**) (1.8 g, 7.69 mmol) in ether (2 ml) at room temperature as described for (**5a**) followed by a similar work-up gave the *title compound* (**5c**) as a bright yellow solid (571 mg, 41%), m.p. 150—153 °C (Found: C, 76.8; H, 5.7; N, 5.25. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.7; N, 5.3%); $\nu_{max.}$(Nujol) 3 280, 3 150br, 1 690, 1 628, 1 611, 1 552, 1 320, 1 230, 750, 740, and 666 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 1.44—1.56 (2 H, m), 1.70—1.83 (2 H, m), 2.21 (2 H, dt, *J* 6.8 and 2.5 Hz), 2.78 (1 H, t, *J* 2.5 Hz), 2.82 (2 H, t, *J* 6.8 Hz), 6.56 (1 H, s), 7.00 (1 H, ~t, *J* 7.8 Hz), 7.20 (1 H, d, *J* 7.8 Hz), 7.50 (1 H, ~t, *J* 7.5 Hz), 7.98 (1 H, d, *J* 7.8 Hz), and 10.48 (1 H, br, NH); *m/z* 265 (M^+, 100%), 221 (77), 198 (50), and 193 (87).

1,2,3,4-*Tetrahydro*-11H-*benzo*[a]*carbazole* (**6c**).—A solution of the pyranoindolone (**5c**) (99 mg, 0.37 mmol) in bromobenzene (10 ml) was heated under reflux under nitrogen for 4 h. The solvent was evaporated off and the residue chromatographed to give the title compound (**6c**) (44 mg, 53%), m.p. 163—165 °C (lit.,[5a] 164—165 °C, lit.,[5b] 115—117 °C) (Found: C, 86.6; H, 6.8; N, 6.3. Calc. for $C_{16}H_{15}N$: C, 86.8; H, 6.8; N, 6.3%); $\nu_{max.}$(Nujol) 3 440, 765, 747, and 734 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.84—2.02 (4 H, m), 2.90 (2 H, t, *J* 6.6 Hz), 2.94 (2 H, t, *J* 6.6 Hz), 6.98 (1 H, d, *J* 7.8 Hz), 7.20 (1 H, ddd, *J* 7.5, 7.5, and 1.5 Hz), 7.35 (1 H, ddd, *J* 7.5, 7.5, and 1.5 Hz), 7.43 (1 H, d, *J* 7.5 Hz) 7.81 (1 H, d, *J* 7.8 Hz), 7.89 (1 H, br, NH), and 8.01 (1 H, d, *J* 7.5 Hz); *m/z* 221 (M^+, 100%), 193 (46), and 28 (40).

7-*Methoxycarbonylhept*-6-*ynoic Acid* (**3d**).—A solution of 7-t-butyldimethylsiloxyhept-1-yne (12 g, 53.1 mmol) in THF (130 ml) was cooled to −78 °C under nitrogen. Butyl-lithium in hexane (1.6M; 36.5 ml, 58.4 mmol) was added over 20 min. The reaction mixture was allowed to warm to −20 °C over 1 h and then recooled to −78 °C. Methyl chloroformate (7.53 g, 79.6

* The use of dimethylformamide as a solvent for sodium acetylide reactions is described in T. F. Rutledge, *J. Org. Chem.*, 1959, **24**, 840.

mmol, 6.15 ml) was added at a rate such that the internal temperature of the reaction mixture did not rise above −40 °C. The reaction was allowed to warm slowly to room temperature overnight. Saturated aqueous ammonium chloride was added and the mixture was extracted twice with ether. The organic extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give essentially pure methyl 8-t-butyldimethylsiloxyoct-2-ynoate (14.8 g), $\nu_{max.}$(film) 2 239, 1 719, 1 255, 1 099, 836, and 776 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.04 (6 H, s), 0.88 (9 H, s), 1.25—1.81 (6 H, m), 2.33 (2 H, t, *J* 7 Hz), 3.59 (2 H, t, *J* 6.5 Hz), and 3.74 (3 H, s); *m/z* 269 ($M^+ - CH_3$, 1%), 253 (2), 227 (28), and 69 (100).

The above crude product was treated with acetic acid–THF–water (3:1:1; 100 ml) and the mixture heated at 80—90 °C for 2 h. The reaction mixture was diluted with water and then neutralised with solid sodium hydrogen carbonate. The neutral mixture was extracted with ether and the organic extracts washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow liquid which consisted of methyl 8-hydroxyoct-2-ynoate and silyl derivatives.

The above crude product was dissolved in acetone (70 ml), cooled to 0 °C, and treated with Jones reagent until the orange colour of the oxidant persisted. The reaction was stirred for a further 60 min and then diluted with water (150 ml). The mixture was extracted with ether and the combined ethereal extracts back extracted with aqueous sodium carbonate (half saturated; 2 × 80 ml). The sodium carbonate extracts were acidified with dilute hydrochloric acid (2M), and extracted with ether. The combined ethereal extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give a yellow oil which was chromatographed on silica (ether–light petroleum) to give the *title compound* (**3d**) as a colourless oil (4.01 g, 41%) (Found: C, 58.6; H, 6.6. $C_9H_{12}O_4$ requires C, 58.7; H, 6.6%); $\nu_{max.}$(film) 3 600—2 500br, 2 238, 1 713, 1 436, 1 258, 1 097, and 753 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.53—1.76 (4 H, m), 2.29—2.37 (4 H, m), 3.70 (3 H, s), and 10.78 (1 H, br s, CO_2H); *m/z* 166 ($M^+ - H_2O$, 5%), 165 (5), 155 (24), 153 (21), 134 (26), 125 (27), 111 (76), 106 (9), and 79 (100).

Bis(7-*methoxycarbonylhept*-6-*ynoic*) *Anhydride* (**4d**).—Prepared as described for (**4a**) in 99% yield. The anhydride was sufficiently pure for subsequent reactions without distillation, $\nu_{max.}$(film) 2 237, 1 817, 1 713, 1 436, 1 259, 1 080, 1 036, and 753 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.56—1.83 (8 H, m), 2.35 (4 H, t, *J* 6.6 Hz), 2.46 (4 H, t, *J* 7 Hz), and 3.72 (6 H, s).

1-(6-*Methoxycarbonylhex*-5-*ynyl*)*pyrano*[3,-b]*indol*-3-*one* (**5d**).—Addition of freshly distilled boron trifluoride–diethyl ether (1.1 ml) to a stirred solution of indol-3-ylacetic acid (1.01 g, 5.77 mmol) and bis(7-methoxycarbonylhept-6-ynoic) anhydride (**4d**) (2.90 g. 8.29 mmol) in ether (5 ml) at 0 °C as described for (**5a**) followed by a similar work-up and chromatography gave the *title compound* (**5d**) as a bright yellow solid (628 mg, 34%), m.p. 147—151 °C (Found: C, 70.6; H, 5.2; N, 4.6. $C_{19}H_{17}NO_4$ requires C, 70.6; H, 5.3; N, 4.3%); $\nu_{max.}$(Nujol) 3 247, 2 235, 1 706, 1 693, 1 632, 1 614, 1 565, and 1 261 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 1.5—1.62 (2 H, m), 1.7—1.82 (2 H, m), 2.48 (2 H, t, *J* 7 Hz), 2.83 (2 H, t, *J* 7 Hz), 3.67 (3 H, s), 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 10.44 (1 H, br NH); *m/z* 323 (M^+, 8%) and 279 (100).

Methyl 1,2,3,4-*Tetrahydro*-11H-*benzo*[a]*carbazole*-5-*carboxylate* (**6d**).—A solution of the pyranoindolone (**5d**) (118 mg, 0.27 mmol) in bromobenzene (25 ml) was heated under reflux under nitrogen for 2.5 h. The solvent was evaporated off and the residue chromatographed (dichloromethane–light petroleum) to give the *title compound* (**6d**) (64 mg, 63%), m.p. 136—137 °C (Found: C, 77.6; H, 6.2; N, 5.1. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $\nu_{max.}$(Nujol) 3 378, 1 694, 1 609, 1 497, 1 436, 1 336, 1 238, 1 191, 1 134, and 729 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.8—1.97 (4 H, m), 2.87 (2 H, t, *J* 6.1 Hz), 3.24 (2 H, t, *J* 6.0 Hz), 3.94 (3 H, s), 7.21—7.27 (1 H, m), 7.36—7.45 (2 H, m), 8.03 (1 H, d, *J* 8 Hz), 8.10 (1 H, br s, NH), and 8.54 (1 H, s, 4-H); *m/z* 279 (M^+, 100%).

Oct-7-*ynoic Acid* (**3e**).—A mixture of 6-chloro-1-t-butyldimethylsiloxyhexane (24.95 g, 99.6 mmol) and sodium iodide (32.82 g, 219.1 mmol) in acetone (175 ml) was heated under reflux under nitrogen for 36 h. The acetone was evaporated off under reduced pressure and water (150 ml) was added. The aqueous mixture was extracted with ether and the combined ethereal extracts washed with aqueous sodium sulphite solution (5%; 50 ml), water, and brine and dried ($MgSO_4$). Evaporation of the solvent gave essentially pure 1-t-butyldimethylsiloxy-6-iodohexane as a pale yellow liquid (34.1 g), $\nu_{max.}$(film) 1 470, 1 460, 1 258, 1 100, 835, and 775 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 0.06 (6 H, s), 0.91 (9 H, s), 1.25—2.03 (8 H, m), 3.21 (2 H, t, *J* 7 Hz), and 3.63 (2 H, t, *J* 6 Hz).

The above crude product (34 g) in DMF (100 ml) was added to a suspension of sodium acetylide (10 g, 210 mmol) in DMF (100 ml) over 15 min at 0 °C. The reaction mixture was stirred at room temperature for 2 h, and then carefully poured into an ice–water mixture (200 g). The aqueous mixture was extracted with ether and the combined ethereal extracts washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure to give 1-t-butyldimethylsiloxyoct-7-yne (21.1 g), $\nu_{max.}$(film) 3 320, 2 120, 1 460, 1 255, 1 100, 840, 780, and 630 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 0.08 (6 H, s), 0.93 (9 H, s), 1.31—1.68 (8 H, m), 1.97 (1 H, t, *J* ~2 Hz), 2.11—2.33 (2 H, m), and 3.64 (2 H, t, *J* 6 Hz).

The above crude product was treated with acetic acid–THF–water (3:1:1; 200 ml), and the mixture heated at 80—90 °C for 2 h. The reaction mixture was then poured into aqueous sodium hydroxide (4M; 500 ml), and the aqueous mixture extracted with ether. The combined ethereal extracts were washed with water and brine, dried ($MgSO_4$), the solvent was evaporated off under reduced pressure, and the residue distilled to give *oct*-7-*yn*-1-*ol* (9.36 g, 75%) as a colourless liquid, b.p. 90—94 °C at ~4 mmHg (Found: C, 76.2; H, 11.4. $C_8H_{14}O$ requires C, 76.1; H, 11.2%); $\nu_{max.}$(film) 3 360br, 3 300, 2 120, and 1 055 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.24—1.57 (8 H, m), 1.90 (1 H, t, *J* 2.5 Hz), 2.13 (2 H, dt, *J* 6.6 and 2.5 Hz), 2.18 (1 H, br), and 3.57 (2 H, t, *J* 6.8 Hz).

The above alcohol (9.36 g, 74.3 mmol) was oxidised as described for compound (**3a**) to give the title compound (**3e**) (5.92 g, 57%), b.p. 96—97 °C at 0.4 mmHg (lit.,[12] b.p. 97—97.5 °C at 1 mmHg), $\nu_{max.}$(film) 3 320, 3 200—3 400, 2 120, and 1 708 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.37—1.77 (6 H, m), 1.92 (1 H, t, *J* 2.5 Hz), 2.18 (2 H, dt, *J* 7.0 and 2.5 Hz), 2.35 (2 H, t, *J* 7.7 Hz), and 8.2 (1 H, br); *m/z* 95 [($M^+ - CO_2H$), 53%], 80 (100), and 55 (87).

Oct-7-*ynoic Anhydride* (**4e**).—This was prepared exactly as described for (**4a**) in 77% yield, b.p. 160—166 °C at 1 mmHg (Found: C, 73.3; H, 8.55. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.45%); $\nu_{max.}$(film) 3 300, 2 115, 1 818, 1 748, and 1 035br cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.38—1.73 (12 H, m), 1.94 (2 H, t, *J* 2.5 Hz), 2.20 (4 H, dt, *J* 6.3 and 2.5 Hz), and 2.46 (4 H, t, *J* 7.1 Hz).

1-(*Hept*-6-*ynyl*)*pyrano*[3,4-b]*indol*-3-*one* (**5e**).—Addition of freshly distilled boron trifluoride–diethyl ether (1 ml) to a stirred solution of indol-3-ylacetic acid (1.01 g, 5.77 mmol) and oct-7-ynoic anhydride (**4e**) (2.01 g, 7.67 mmol) in ether (1 ml) at room temperature as described for (**5a**) followed by a similar work-up and chromatography gave the *title compound* (**5e**) as a bright yellow solid (471 mg, 29%), m.p. 187—191 °C (Found: C, 77.4;

H, 6.1; N, 5.0. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $\nu_{max.}$(Nujol) 3 245br, 1 690, 1 630, 1 611, 1 560, 1 322, and 740 cm^{-1}; δ_H[250 MHz; $(CD_3)_2SO$] 1.36—1.55 (4 H, m), 1.63—1.75 (2 H, m), 2.15 (2 H, dt, *J* 6.4, 2.5 Hz), 2.74 (1 H, t, *J* 2.5 Hz), 2.81 (2 H, t, *J* 7.3 Hz), 6.54 (1 H, s), 7.00 (1 H, ~t, *J* 7.8 Hz), 7.20 (1 H, d, *J* 7.8 Hz), 7.50 (1 H, ~t, *J* 7.8 Hz), 7.97 (1 H, d, *J* 7.8 Hz), and 10.47 (1 H, br, NH); *m/z* 279 (M^+, 100%), 235 (30), 198 (61), and 184 (43).

2,3,4,5-*Tetrahydro*-1H,12H-*cyclohepta*[a]*carbazole* (**6e**).—A solution of the pyranoindolone (**5e**) (54 mg, 0.19 mmol) in benzonitrile (8 ml) was heated under reflux under nitrogen for 14 h. The solvent was evaporated and the residue chromatographed to give the *title compound* (**6e**) (15.7 mg, 35%), m.p. 151—154 °C (Found: C, 86.85; H, 7.3; N, 5.9. $C_{17}H_{17}N$ requires C, 86.8; H, 7.3; N, 5.95%); $\nu_{max.}$(Nujol) 3 426, 770, 742, and 667 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.65—1.78 (4 H, m), 1.87—1.97 (2 H, m), 2.94—3.01 (4 H, m), 7.02 (1 H, d, *J* 7.8 Hz), 7.18 (1 H, ddd, *J* 7.5, 7.5, and 1.6 Hz), 7.32—7.42 (2 H, m), 7.78 (1 H, d, *J* 7.8 Hz), 7.93 (1 H, br, NH), and 8.01 (1 H, d, *J* 7.5 Hz); *m/z* 235 (M^+, 100%), 206 (24), 194 (11), 180 (13), and 28 (66).

Methyl 2-(*Hex*-5-*ynoyl*)*indol*-3-*ylacetate* (**7a**).—Oxalyl chloride (423 mg, 3.33 mmol, 0.29 ml) was added to a stirred solution of hex-5-ynoic acid (**3a**) (249 mg, 2.22 mmol) in dry ether (15 ml) and the reaction mixture was stirred at room temperature for 12 h. The mixture was concentrated under reduced pressure and the residue dissolved in dry dichloromethane (25 ml) under nitrogen. Zinc chloride (900 mg, 6.6 mmol) was added followed by a solution of methyl indol-3-ylacetate (400 mg, 2.12 mmol) in dichloromethane (5 ml). After 1.5 h the reaction mixture was poured into dilute hydrochloric acid (1M; 100 ml) and extracted with ether. The organic extracts were washed with saturated aqueous sodium hydrogen carbonate, water, brine, and dried ($MgSO_4$). The solvent was evaporated off and the residue chromatographed (ether–light petroleum) to give the *title compound* (**7a**) (322 mg, 54%), m.p. 124—125 °C (Found: C, 72.1; H, 6.0; N, 4.9. $C_{17}H_{17}NO_3$ requires C, 72.1; H, 6.05; N, 4.9%); $\nu_{max.}$(Nujol) 3 325, 3 295, 3 260, 1 710, 1 660, 1 535, 1 210, 750, 740, and 670 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.83—1.94 (2 H, m), 1.97 (1 H, t, *J* 2.5 Hz), 2.28 (2 H, dt, *J* 6.5 and 2.5 Hz), 2.95 (2 H, t, *J* 7 Hz), 3.72 (3 H, s), 4.15 (2 H, s), 7.11—7.18 (1 H, m), 7.28—7.35 (2 H, m), 7.66 (1 H, d, *J* 8 Hz), and 9.18 (1 H, br, NH); *m/z* 283 (M^+, 100%), 252 (3), 251 (3), 231 (17), and 224 (59).

2-(*Hex*-5-*ynoyl*)*indol*-3-*ylacetic Acid* (**8a**).—Aqueous potassium hydroxide (2M; 6 ml) was added to a stirred solution of methyl 2-(hex-5-ynoyl)indol-3-ylacetate (**7a**) (287 mg, 1.01 mmol) in THF–methanol (9:1; 10 ml). The reaction was stirred for 2 h and then diluted with water (50 ml) and the basic mixture was extracted with ether (50 ml). The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether. The combined ether extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give the *title compound* (**8a**) (267 mg, 98%), m.p. 171—172 °C (Found: C, 71.6; H, 5.6; N, 5.2. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%); $\nu_{max.}$(Nujol) 3 335, 3 300, 3 280, 1 700, 1 650, 1 535, 1 025, and 750 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.95—2.06 (3 H, m), 2.36 (2 H, dt, *J* 6.6 and 2.5 Hz), 3.34 (2 H, t, *J* 7 Hz), 4.15 (2 H, s), 7.16—7.23 (1 H, m), 7.33—7.40 (2 H, m), 7.74 (1 H, d, *J* 8.3 Hz), and 9.02 (1 H, br, NH); *m/z* 269 (M^+, 100%), 225 (37), 224 (40), 156 (31), 130 (34), and 128 (31).

2,3-*Dihydro*-1H,10H-*cyclopenta*[a]*carbazole* (**6a**).—A solution of 2-(hex-5-ynoyl)indol-3-ylacetic acid (**8a**) (42 mg, 0.16 mmol) in acetic anhydride (20 ml) was heated under reflux nitrogen for 3 h. The mixture was evaporated and the residue chromatographed to give the title compound (**6a**) (18 mg, 56%) with identical ^1H n.m.r. and t.l.c. properties to the previous sample described above.

Methyl 2-(*Oct*-7-*ynoyl*)*indol*-3-*ylacetate* (**7b**).—Oxalyl chloride (174 mg, 1.37 mmol, 0.12 ml) was added to a stirred solution of oct-7-ynoic acid (**3e**) (128 mg, 0.91 mmol) in dry ether (10 ml) and the reaction allowed to stir at room temperature for 12 h. The mixture was concentrated under reduced pressure and the residue dissolved in dry dichloromethane (20 ml) under nitrogen. Zinc chloride (377 mg, 2.76 mmol) was added followed by a solution of methyl indol-3-ylacetate (160 mg, 0.85 mmol) in dichloromethane (2 ml). After 1 h the reaction mixture was poured into dilute hydrochloric acid (1M; 50 ml) and extracted with ether. The organic extracts were washed with saturated aqueous sodium hydrogen carbonate, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether–light petroleum) to give the *title compound* (**7b**) (174 mg, 66%), m.p. 94—95 °C (Found: C, 73.0; H, 6.8; N, 4.5. $C_{19}H_{21}NO_3$ requires C, 72.3; H, 6.8; N, 4.5%); $\nu_{max.}$(Nujol) 3 328, 3 266, 1 735, 1 650, 1 535, 1 329, and 1 195 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.44—1.65 (4 H, m), 1.71—1.82 (2 H, m), 1.95 (1 H, t, *J* 2.3 Hz), 2.22 (2 H, dt, *J* 7 and 2.3 Hz), 2.93 (2 H, t, *J* 7 Hz), 3.66 (3 H, s), 4.08 (2 H, s), 7.17 (1 H, ddd, *J* 7, 8, and 2.1 Hz), 7.31—7.40 (2 H, m), 7.69 (1 H. dd, *J* 8 and 2.1 Hz), and 9.08 (1 H, br, NH); *m/z* 311 (M^+, 100%), 279 (12), and 252 (20).

2-(*Oct*-7-*ynoyl*)*indol*-3-*ylacetic Acid* (**8b**).—Aqueous potassium hydroxide (2M; 3 ml) was added to a stirred solution of methyl 2-(oct-7-ynoyl)indol-3-ylacetate (**7b**) (120 mg, 0.39 mmol) in THF–water–methanol (9:2:1; 10 ml). The reaction was stirred for 1 h and then diluted with water (50 ml) and the basic mixture was extracted with ether (50 ml). The aqueous phase was acidified with dilute hydrochloric acid and extracted with ether. The combined ether extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to give the *title compound* (**8b**) (111 mg, 97%), m.p. 176—178 °C (Found: C, 72.6; H, 6.4; N, 4.75. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.4; N, 4.7%); $\nu_{max.}$(Nujol) 3 314, 3 282, 1 698, 1 648, 1 532, 1 420, 1 349, 1 226, 1 209, 1 021, and 746 cm^{-1}; δ_H[270 MHz; $(CD_3)_2CO$] 1.40—1.62 (4 H, m), 1.68—1.79 (2 H, m), 2.18 (2 H, dt, *J* 7 and 2.5 Hz), 2.30 (1 H, t, *J* 2.5 Hz), 3.04 (2 H, t, *J* 7.4 Hz), 4.20 (2 H, s), 7.11 (1 H, ~t, *J* 7.9 Hz), 7.30 (1 H, ~t, *J* 7.9 Hz), 7.47 (1 H, d, *J* 7.9 Hz). 7.74 (1 H, d, *J* 7.9 Hz), and 10.67 (1 H, br NH); *m/z* 297 (M^+, 100%), 253 (43), 238 (20), 217 (25), 196 (25), 158 (80), and 130 (65).

2,3,4,5-*Tetrahydro*-1H,12H-*cyclohepta*[a]*carbazole* (**6e**).—A solution of 2-(oct-7-ynoyl)indol-3-ylacetic acid (**8b**) (102 mg, 0.34 mmol) in butyric anhydride (25 ml) was heated under reflux under nitrogen for 18 h. The mixture was evaporated and the residue chromatographed to give the title compound (**6e**) (20 mg, 25%) with identical ^1H n.m.r. and t.l.c. properties to the previous sample described above.

Hex-5-*enoic Acid.*—Jones reagent was added to a stirred solution of hex-5-en-1-ol (5.41 g, 54.1 mmol) in acetone (55 ml), with external cooling until the orange colour of the oxidant persisted. Work-up and isolation as described for compound (**3a**) gave the title compound (4.16 g, 67%), b.p. 68 °C at 0.6 mmHg (lit.,[7] b.p. 101—104 °C at 12 mmHg), $\nu_{max.}$(film) 3 400—2 400br, 1 709, 1 643, 1 416, 1 246, 1 209, 994, and 915 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.66—1.78 (2 H, m), 2.05—2.13 (2 H, m), 2.34 (2 H, t, *J* 7.5 Hz), 4.95—5.06 (2 H, m), 5.68—5.84 (1 H, m), and 11.33 (1 H, br s, CO_2H).

Hex-5-*enoic Anhydride.*—This was prepared as described for (**4a**) in 92% yield. The anhydride was sufficiently pure for subsequent reactions without distillation, $\nu_{max.}$(film) 1 819,

1 751, 1 642, 1 039, and 915 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.67—1.9 (4 H, m), 2.02—2.25 (4 H, m), 2.46 (4 H, t, *J* 7 Hz), 4.90—5.20 (4 H, m), and 5.57—6.02 (2 H, m).

1-(*Pent-4-enyl*)*pyrano*[3,4-b]*indol-3-one* (**9**).—Addition of freshly distilled boron trifluoride–diethyl ether (2 ml) to a stirred solution of indol-3-ylacetic acid (2.00 g, 11.43 mmol) and hex-5-enoic anhydride (3.27 g, 15.57 mmol) in ether (3 ml) at 0 °C as described for (**5a**) followed by a similar work-up gave the *title compound* (**9**) as a bright yellow solid (1.29 g, 45%), m.p. 139—141 °C (decomp.) (Found: C, 75.7; H, 5.9; N, 5.5. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); $\nu_{max.}$(Nujol) 3 143, 1 694, 1 628, 1 613, 1 562, 1 323, 1 228, 1 151, 744, and 731 cm^{-1}; δ_H [250 MHz; $(CD_3)_2SO$] 1.75—1.87 (2 H, m), 2.09—2.18 (2 H, m), 2.85 (2 H, t, *J* 7.5 Hz), 4.78—4.91 (2 H, m), 5.59—5.75 (1 H, m), 6.55 (1 H, s), 6.99 (1 H, ~t, *J* 8 Hz), 7.20 (1 H, d, *J* 8 Hz), 7.49 (1 H, ~t, *J* 8 Hz), 7.96 (1 H, d, *J* 8 Hz), and 10.44 (1 H, br, NH); *m/z* 253 (M^+, 8%), 209 (65), 208 (25), 207 (22), 180 (100), and 44 (51).

2,3-*Dihydro*-1H,10H-*cyclopenta*[a]*carbazole* (**6a**).—(*a*) A solution of the pyranoindolone (**9**) (108 mg, 0.43 mmol) in bromobenzene (20 ml) was heated under reflux under nitrogen for 1.5 h. The solvent was evaporated off and the residue chromatographed to give the title compound (**6a**) (14 mg, 16%) with identical ^1H n.m.r. and t.l.c. properties to the previous sample described above.

(*b*) A mixture of the pyranoindolone (**9**) (73 mg, 0.29 mmol) and palladium–carbon (10%; 65 mg) in bromobenzene (10 ml) was heated under reflux for 1.5 h. The hot mixture was filtered through a pad of silica and the residue washed well with ethyl acetate. The filtrate was concentrated and the residue chromatographed to give the title compound (**6a**) (26 mg, 43%) with identical ^1H n.m.r. and t.l.c. properties to the previous sample described above.

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References

1 Part 2, C. J. Moody and P. Shah, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1407.
2 C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2505.
3 E. R. Marinelli, *Tetrahedron Lett.*, 1982, **23**, 2745.
4 Preliminary communication, C. J. Moody, P. Shah, and P. Knowles, *Tetrahedron Lett.*, 1988, **29**, 2693.
5 (*a*) R. J. Olsen and W. Cummings, *J. Heterocycl. Chem.*, 1981, **18**, 439; (*b*) S. Kano, E. Sugino, S. Shibuya, and S. Hibino, *J. Org. Chem.*, 1981, **46**, 3856.
6 A. G. Fallis, *Can. J. Chem.*, 1984, **62**, 183.
7 R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1934, 1995.
8 R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1957, 1435.
9 W. P. Jackson, Ph.D. Thesis, University of London, 1981; *cf.* J. Drouin, F. Leyendecker, and J. M. Conia, *Tetrahedron Lett.*, 1975, 4053.
10 W. R. Taylor and F. M. Strong, *J. Am. Chem. Soc.*, 1950, **72**, 4263.

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