# Addition Reactions of Heterocyclic Compounds. Part 75.[1] Reactions of Dimethyl Acetylenedicarboxylate with some *N*-Methylindoles

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4-Methyl-1,2,3,4-tetrahydrocyclopent[*b*]indole, 5-methyl-1,2,3,4-tetrahydrocarbazole, and 5-methyl-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole were treated with dimethyl acetylenedicarboxylate in aqueous solvents. Lactones derived from the 2,3-dihydroindole system were obtained in all cases, and a diketone possessing the phenanthridone nucleus was also obtained from the carbazole. The products were identified from ¹H and ¹³C n.m.r. spectral comparisons, and in some cases from ¹³C–¹H coupling constants observed in the ¹³C spectra.

THE strained indoles (1) and (2) are hydrolysed by acid, like enamines, to the corresponding amino-ketones.[2] With dimethyl acetylenedicarboxylate (DMAD) in wet solvents several types of transformation occur, involving opening of the unsaturated nitrogen-containing ring, leading to unusual structures which have been identified in some cases by X-ray crystallography. This investigation has now been extended to the indoles (3)—(5), lacking the ethano bridge, which unlike (1) and (2) are
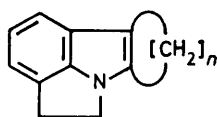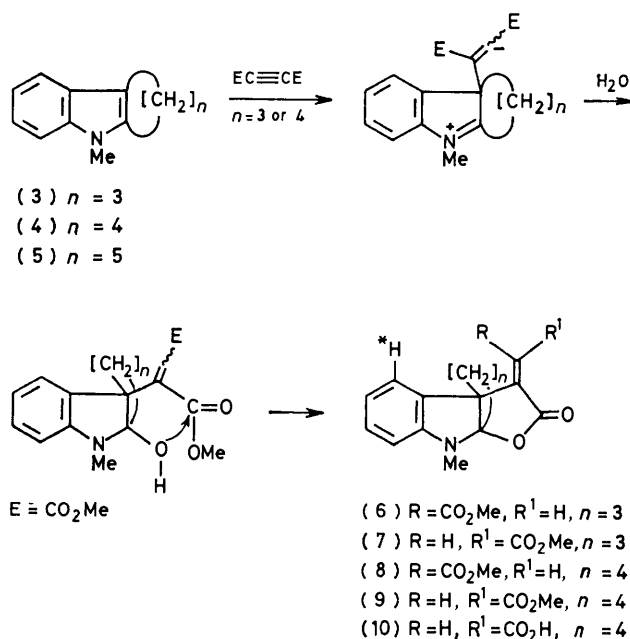

(1) *n* = 4
(2) *n* = 5

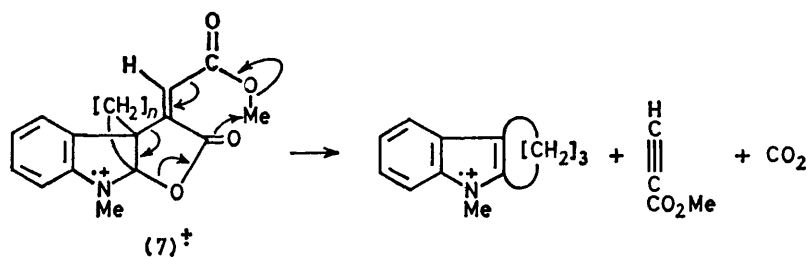not hydrolysed to amino-ketones under similar conditions.

The indole (3) with DMAD in methanol or acetic acid gave orange (A) and yellow (B) adducts having very similar u.v. spectra and the composition required of structures (6), (7), and (11). Their fully proton-decoupled ¹³C n.m.r. spectra (Table) showed differences of 2.6 p.p.m. or less for all corresponding resonances except for one sp^2-hybridised atom and the lactone *C*=O atoms. A number of resonances can be assigned by comparison with those of indole and 5-ethylcarbazole.[3] In the non-proton-decoupled spectra the lactone *C*=O atoms gave rise to doublets with *J* 7.2 and 12.5 Hz, respectively. This defines compounds A and B as having structures (6) and (7), respectively, since structures where the interacting hydrogen and carbon atoms are *cis* have coupling constants in the 5—7 Hz region, whereas values for those with the *trans* arrangement are between 11.5 and 12.2 Hz.[4,5] Structure (11) is excluded as no significant coupling was observed [1,4] between the carbonyl carbon atom and the neighbouring olefinic hydrogen atom in some related lactams, and the corresponding coupling for (12) is 2.9 Hz. The only other significant difference between the ¹³C spectra of A and B is the resonance of the sp^2-hybridised atom of the lactone ring, which is 7.1 p.p.m. towards lower field (at δ 147.8) for A (6), and this can be associated with the increased steric strain.

In agreement with these conclusions, the ¹H n.m.r. spectrum of compound A (6) shows a lower-field olefinic proton than that of B (7), which is comparable to those of diethyl fumarate (δ 6.83) and maleate (δ 6.28),[6] and a low-field (δ 7.61) aromatic one-proton multiplet absent from the spectrum of compound B. This multiplet is due to the proximity of the ester-carbonyl to the proton marked with an asterisk in the displayed structure. The i.r. maxima shown by A (1 755 and 1 733 cm⁻¹) and B (1 745—1 720 cm⁻¹) are very close to, or in the ranges quoted[7] for, αβ-unsaturated and aryl esters (1 730—1 717 cm⁻¹) and αβ-unsaturated five-membered lactones (1 760—1 740 cm⁻¹). The mass spectra of A and B showed the molecular ions as the base peaks, but whereas A gave only two significant fragments, both of low intensity and which could not be convincingly accounted for, B gave daughter ions consistent with its proposed stereochemistry and the fragmentation as shown in Scheme 2. Compounds (6) and (7) could be formed by electrophilic attack at position 3 of the original indoles, followed by the other reactions shown in Scheme 1.

(3) *n* = 3
(4) *n* = 4
(5) *n* = 5

E ≡ CO₂Me

(6) R = CO₂Me, R¹ = H, *n* = 3
(7) R = H, R¹ = CO₂Me, *n* = 3
(8) R = CO₂Me, R¹ = H, *n* = 4
(9) R = H, R¹ = CO₂Me, *n* = 4
(10) R = H, R¹ = CO₂H, *n* = 4

SCHEME 1

The carbazole (4) with DMAD in wet methanol gave the adduct (8) and two further products (C and D). Compound (8) had spectra (including the ^{13}C n.m.r. carbonyl multiplicity) very similar to those of (6), the only significant differences being in the slightly higher field resonances of the bridgehead sp^3-hybridised carbon atoms and the sp^2-C of the lactone ring at δ 144.2 (Table).

one CH_2 group of the tetramethylene bridge of the original carbazole (4) had been replaced by another resonating at significantly lower field (δ 35.6). The special features of the ^{1}H n.m.r. spectrum are the presence of an uncoupled olefinic proton (δ 6.10) suggesting [6] a *cis* arrangement of ester groups on a double bond, and two apparent one-proton singlets at δ 3.40 and 3.43 which are assigned to
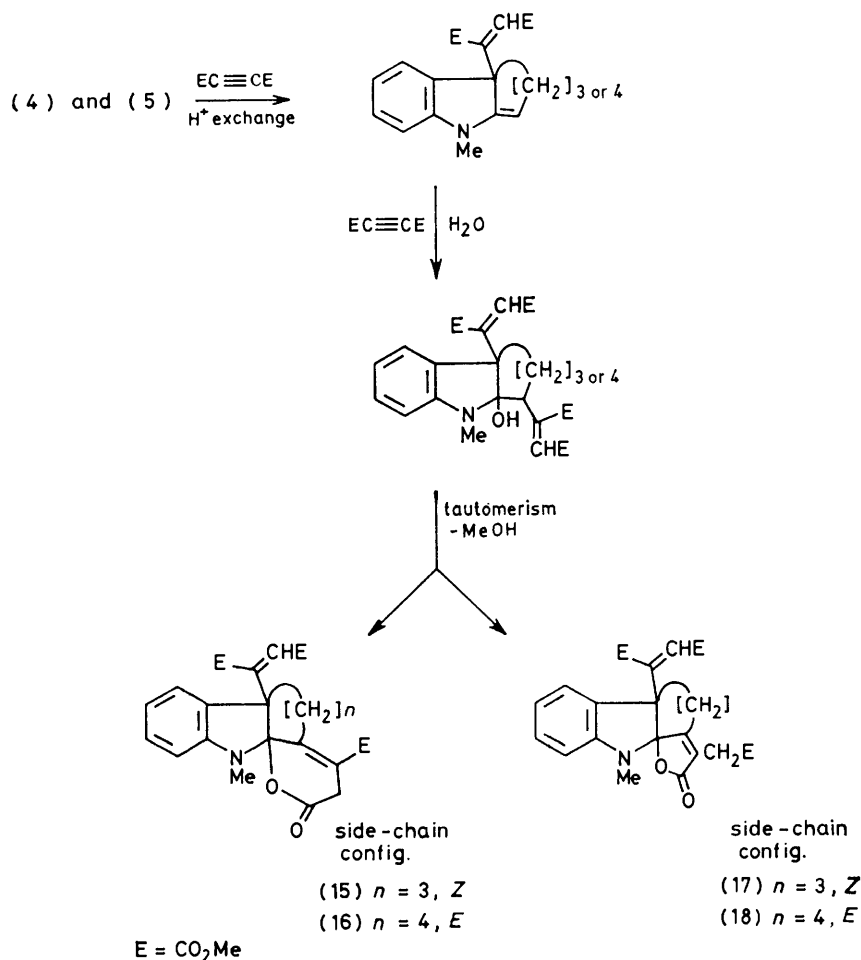

SCHEME 2

Compound C, from its spectra, is clearly very closely related to the isomeric compound (8), but shows some significant differences. The i.r. carbonyl maxima are broader, and at lower wave numbers, and the ^{13}C n.m.r. spectrum shows the signal due to the bridgehead sp^3-hybridised carbon atom, which is attached to three other carbon atoms, at higher field than that of (8). The lactone-carbonyl signal is also at higher field, and in total contrast to that of (8) shows weak coupling with the olefinic proton. The ester-carbonyl carbon atom couples much more strongly (6.2 Hz) than that of (8) (1.2 Hz), and the value of the coupling constant indicates vicinal coupling with a *cis* arrangement of the interacting groups. These differences are readily accommodated if compound C has structure (12); this is consistent with the presence of a lowish field aromatic proton signal (δ 7.42) due to the proton marked with an asterisk being affected by the nearby ester group, and with the fact that the molecule fragments more easily than (6), (7) or (8). The molecular ion (43%) is not the base peak, which in fact corresponds to the loss of the elements of carbon dioxide and methyl propiolate from the molecular ion, no rearrangement (contrast Scheme 2) being necessary.

In wet acetic acid the carbazole (4) with DMAD gave compound (13) as the major product. It was identified from the similarities in its i.r., u.v., mass, and ^{1}H and ^{13}C n.m.r. spectra to those [2] of (14), the structure of which was established by X-ray crystallography,[8] and could be formed in the same way. However the amide-carbonyl in (13) is coupled to the N-methyl protons ($^3J_{CO, CH_3}$ 2.7 Hz), whereas in (14) no $^3J_{CO, NCH_3}$ coupling is observed.[5] A similar observation was made by von Philipsborn in a study of five-membered heterocycles.[4] Minor products were D, and an acid E. Compound D is formed by the carbazole adding two moles of DMAD and losing ' CH_2 '. The ^{13}C spectrum showed three CO_2CH_3 groups, a lactone $C=O$ group at lower field consistent with the i.r. maximum at 1 757 cm^{-1}, and many similarities to the spectra of (8) and (12). Apart from the expected differences due to the alteration in molecular composition,

the methylene group α to a carbonyl function because of their low-field position. These protons should appear as a singlet, or as an AB type of spectrum because of their diastereotopic nature, but the outer lines were too small to be differentiated from the instrumental noise. However on adding the shift reagent Eu(fod)$_3$ the resonances due to this methylene group were strongly affected and a double doublet with a 17 Hz coupling constant characteristic of such a group developed. The

(11) n = 3
(12) n = 4

(13) R = Me, R^1 = H
(14) R—R^1 = CH$_2$CH$_2$

E = CO$_2$Me
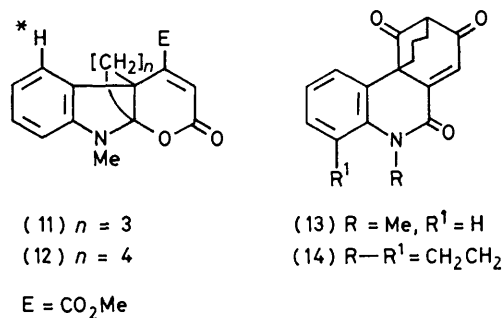
non-proton-decoupled ^{13}C spectrum revealed the lactone carbon signal as a triplet (coupled to the methylene protons) and showed that one of the ester-carbonyls was strongly coupled (11.6 Hz), and another weakly coupled (1.4 Hz), to the olefinic proton, confirming a *cis*-arrangement of these ester groups. The remaining ester-carbonyl was also coupled to the methylene group. The structure for D which agrees best with these data is (15) [or (17)] and could be formed as in Scheme 3.

The acid E has spectra similar to those of (6), (7), (8), and (12), except for those features attributable to a carboxy-group. The non-proton-decoupled ^{13}C spectrum reveals the lactone-carbonyl coupled to the olefinic proton with a coupling constant 13.1 Hz indicating vicinal coupling with a *trans* arrangement of the interacting groups and hence structure (10). Furthermore, methylation with diazomethane gave a methyl ester exhibiting spectra very similar to those of (7) and consistent only with structure (9).

SCHEME 3

Compound F was the only crystalline product from the reaction of cyclohept[*b*]indole (5) and DMAD in wet methanol. It possessed spectra reminiscent of those of D and an analogous molecular formula. The carbonyl frequencies at higher wavenumber are similar, and close to the ranges expected for both αβ-unsaturated five-membered lactones (1 760—1 740 cm⁻¹) and βγ-unsaturated six-membered lactones (1 750—1 735 cm⁻¹).[7] The only significant spectral differences between D and F are (a) F exhibits an olefinic signal at lower field indicating an E-configuration of the side chain ester groups; (b) the largest coupling constant observed among the ester groups of F (8.5 Hz) is much smaller than in D and confirms this E-configuration; and (c) the lowest field CH_2 resonance (δ 3.45) in F is a singlet which moves downfield as a singlet on the addition of Eu(fod)₃. The structural significance of this last difference between F and D is not yet clear. From these data the structure of F appears to be either (16) or (18) and it could be formed as in Scheme 3.

EXPERIMENTAL

The instruments and procedures have been noted previously,[1] except that the ¹³C and ¹H n.m.r. spectra were

recorded using a JEOL FX90Q spectrometer,[5] and the u.v. spectra using a Beckman Acta III spectrometer.

4-Methyl-1,2,3,4-*tetrahydrocyclopent*[b]*indole* (3).— 1-Methyl-1-phenylhydrazine [9] with cyclopentanone, by the method of Perkin,[10] gave the indole (3) in 60% yield, m.p. 43° (from ethanol) (lit.,[10] m.p. 43°); δ 7.55—6.9 (4 H, m, aryl H), 3.52 (3 H, s, NMe), and 3.0—2.2 (6 H, m, 3 CH₂); m/z 171 (M⁺, 100%), 170 (90), and 144 (15).

The Indole (3) *with Dimethyl Acetylenedicarboxylate.*—The indole (3) (5 g) and DMAD (8 g) were mixed in methanol (40 ml) and left at room temperature for 6 days, after which all the indole (3) had been consumed (t.l.c.). Evaporation under reduced pressure and preparative layer chromatography (p.l.c.) (5% methanol–chloroform) gave numerous coloured bands, two of which yielded crystalline material.

(i) The intense orange band (R_f 0.8) gave orange prisms (from ethanol) (3.5 g, 40%) of the adduct (6), m.p. 96—98° (Found: C, 68.5; H, 5.9; N, 4.6. $C_{17}H_{17}NO_4$ requires C, 68.2; H, 5.7; N, 4.7%); $\nu_{max.}$ 3 060—2 800w, 1 755s, 1 733s, 1 665w, and 1 600m cm⁻¹; $\lambda_{max.}$ 238 (ε 15 000) and 292 nm (1 500); m/z 299 (M⁺, 100%), 197 (30), and 168 (15); δ 7.61 (1 H, dd, J 7 and 1.5 Hz), 7.18 (1 H, dt, J 7 and 1.5 Hz), 6.66 (1 H, dt, J 7 and 1.5 Hz), 6.39 (1 H, d, J 7 Hz, not affected by irradiating at 7.61), 6.78 (1 H, s, olefinic H), 3.89 (3 H, s, OMe), 2.96 (3 H, s, NMe), and 2.7— 1.6 (6 H, m, aliphatic H) (unchanged on shaking with D₂O).

(ii) The yellow band (R_f 0.3) gave yellow laths (1.4 g,

^{13}C N.m.r. spectra for solutions in CDCl$_3$ measured at 22.63 MHz and recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted. Coupling constants derived from partially decoupled, or non-decoupled spectra, are indicated by the superscripts

Compounds

Assignments	(6)	(7)	(8)	(9)	(10)	(12)
Lactone CO	169.9s[a]	167.0s[b]	168.6s[c]	165.4s[o]	163.2s[e]	163.0s[d]
CO$_2$	165.2s[f]	165.5s[g]	165.4s[h]	165.6s[r]		165.4s[i]
CO$_2$H					170.5s[p]	
sp^{2}C	149.9s	149.4s	148.5s	148.4s	147.5s	148.5s
	147.8s	140.7s	144.2s	139.4s	142.8s	146.5s
	129.8s	129.6s	131.0s	131.4s	130.5s	129.7s
sp^{2}C–H	129.7d	129.4d	129.4d	129.3d	129.8d	128.8d
	125.6d	127.0d[j]	125.4d[j]	124.6d[j]	129.1d[j]	124.3d
	125.1d[j]	123.0d	125.0d	122.9d	122.9d	124.3d[j]
	119.1d	118.9d	120.0d	120.1d	120.7d	119.9d
	106.0d	106.2d	107.6d	108.5d	108.8d	108.1d
sp^{3}C–N(–O)	115.5s	114.9s	107.6s	107.3s	113.3s	106.2s
sp^{3}C	62.1s	61.7s	55.9s	54.4s	56.2s	48.6s
O–CH$_3$	52.3q	52.4q	52.2q	52.4q		52.5q
N–CH$_3$	28.5q	28.5q	28.1q	28.3q	28.1q	29.3q
sp^{2}CH$_2$	39.4t	40.6t	29.7t	32.1t	31.9t	29.7t
	35.7t	35.9t	29.1t	29.9t	29.7t	27.7t
	25.7t	25.5t	19.7t	21.0t	20.9t	21.8t
			19.3t	20.1t	19.8t	21.3t

Assignments	(13)	(14)	(15) or (17)	(16) or (18)
Ketone CO	203.0s	203.6s		
	197.4s	197.5s		
Amide CO	159.4s[t]	157.1s[k]		
Lactone CO			169.9s[l,m]	171.4s[v]
CO$_2$Me			169.6s[m,g]	169.7s[w]
			167.9s[s]	167.9s[z]
			164.9s[x]	165.4s[y]
sp^{2}C	146.1s	147.5s	159.2s	162.9s
	136.9s	137.8s	148.1s	150.1s
		130.1s	146.6s	142.7s
	121.6s	119.1s	132.7s	128.3s
			123.8s	125.0s
sp^{2}CH	135.0d[j]	134.1d[j]	129.1d	129.5d
	130.2d	127.2d	125.3d[j]	129.1d[j]
	128.9d	124.9d	123.4d	124.6d
	123.4d	124.3d	119.7d	117.6d
	115.2d		108.1d	104.7d
sp^{3}CH	62.5d	62.2d		
sp^{3}C–N(–O)			105.5s	108.6s
sp^{3}C	56.4s	57.7s	59.4s	58.2s
O–CH$_3$			52.5q	52.4q
			52.4q	52.4q
			52.0q	51.7q
N–CH$_3$	30.5q	45.8t[n]	27.1q	26.7q
sp^{3}CH$_2$	40.8t	41.2t	35.6t	36.8t
	32.4t	33.1t	28.8t	28.8t
	16.8t	27.4t	24.8t	26.7t
		16.7t	22.2t	26.7t
				23.6t

[a] d, $^3J_{CO,H}$ 7.2. [b] d, $^3J_{CO,H}$ 12.5. [c] d, $^3J_{CO,H}$ 7.8. [d] d, $^2J_{CO,H}$ 2.9. [e] d, $^3J_{CO,H}$ 13.1. [f] dq, $^3J_{CO,H}$, 4; $^2J_{CO,H}$ 1.2. [g] dq, $^3J_{CO,CH_3}$ 4; $^2J_{CO,H}$ 1.6. [h] dq, $^3J_{CO,CH_3}$ 3.9; $^2J_{CO,H}$ 1.2. [i] dq, $^3J_{CO,CH_3}$ 3.7; $^3J_{CO,H}$ 6.2. [j] Olefinic ≡CH– from the selectively decoupled and non-decoupled spectra. [k] d, $^3J_{CO,H}$ 5.9. [l] t, J_{CO,CH_2} 4.4. [m] Determined by the selective excitation method (G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1977, 433). [n] CH$_2$ resonance. [o] d, $^3J_{CO,H}$ 12.5. [p] s. [q] tq, $^3J_{CO,CH_2}$ J_{CO,CH_3} 3.8. [r] dq, $^3J_{CO,CH_3}$ 4.1; $^2J_{CO,H}$ 1.7. [s] dq, $^3J_{CO,CH_3}$ 4.1; $^3J_{CO, olefin H}$ 11.6. [t] dq, $^3J_{CO, olefin H}$ 5.8; $^3J_{CO, NCH_3}$ 2.7. [u] dq, $^3J_{CO,CH_3}$ 3.8; $^2J_{CO, olefin H}$ 1.2. [v] t, J_{CO,CH_2} 4.9. [w] tq, $^3J_{CO,CH_2}$ J_{CO,CH_3} 4.0. [x] dq, $^3J_{CO,CH_3}$ 4.0; $^3J_{CO, olefin H}$ 8.5. [y] dq, $^3J_{CO,CH_3}$ 3.9; $^2J_{CO, olefin H}$ 0.7.

16% yield) (from ethanol) of the isomeric *adduct* (7), m.p. 147—149° (Found: C, 68.4; H, 5.8; N, 4.7. C$_{17}$H$_{17}$NO$_4$ requires C, 68.2; H, 5.7; N, 4.7%), $\nu_{max.}$ 3 060—2 800w, 1 745—1 720, s, 1 665w, and 1 610w cm^{-1}; $\lambda_{max.}$ 245 (ε 13 200) and 296 nm (1 400); m/z 299 (M^+, 100%), 224 (30), 212 (25), 197 (50), 171 (80), 170 (80), 168 (45), and 151 (30); δ 7.3—6.27 (4 H, m, aryl H), 6.50 (1 H, s, olefinic H), 3.87 (3 H, s, OMe), 2.96 (3 H, s, NMe), and 2.7—1.6 (6 H, m, aliphatic H), unchanged on shaking with D$_2$O.

When the reaction was carried out in either boiling glacial acetic acid (1 day) or in glacial acetic acid at room temper-ature (4 days) the products were again (6) (5%) and (7) (40%).

5-*Methyl*-1,2,3,4-*tetrahydrocarbazole* (4).—Methylation of 1,2,3,4-tetrahydrocarbazole[11] using dimethyl sulphate and phase-transfer catalysis (tetra-n-butylammonium hydrogen sulphate)[12] gave the carbazole (4) (75%), m.p. 50—51° (lit.,[13] 50—51°); m/z 185 (M^+, 100%) and 157 (80); δ 7.68—6.85 (4 H, m, aryl H), 3.55 (3 H, s, NMe), 2.95—2.40 (4 H, m, aliphatic H), and 2.2—1.4 (4 H, m, aliphatic H).

The 5-*Methyltetrahydrocarbazole* (4) *with Dimethyl Acetylene-dicarboxylate*.—(a) The carbazole (4) (1 g) and DMAD

(3 g) were heated under reflux at 100 °C in wet acetic acid (25 ml) for 3 days. Evaporation under reduced pressure and p.l.c. (chloroform) yielded numerous bands of which three afforded crystalline material.

(i) The intense yellow band (R_f 0.5) gave 5-*methyl-9,10,11,12-tetrahydro-9,12a-methanocyclo-octa*[c]*quinoline-6,8,13-trione* (13) (0.35 g) as yellow laths (from ethanol), m.p. 222—223° (Found: C, 72.6; H, 5.3; N, 5.0. $C_{17}H_{15}$-NO_3 requires C, 72.6; H, 5.4; N, 5.0%), $\nu_{max.}$ 1 745s, 1 735infl, 1 670s, and 1 650s cm^{-1}; $\lambda_{max.}$ 236 (ε 14 500) and 360br nm (2 570) unchanged on the addition of one drop of 70% perchloric acid; m/z 281 (M^+, 58%), 225 (62), 224 (23), 213 (18), 210 (22), 197 (100), and 185 (22); δ 7.80—7.00 (5 H, m, aryl H + olefinic H), 3.54 (4 H, s, NMe + COCH-CO), and 2.50—1.50 (6 H, m, 3 $\times$ CH$_2$).

(ii) The pale yellow band (R_f 0.2) which appeared dark blue under u.v. light (254 nm) gave colourless plates (35 mg) (from ethanol) of compound D, m.p. 129—130° (Found: C, 62.9; H, 5.8; N, 3.0. Calc. for $C_{24}H_{25}NO_8$: C, 63.3; H, 5.5; N, 3.1%); $\nu_{max.}$ 1 757s, 1 735s, 1 720s, 1 630w, and 1 605w cm^{-1}; $\lambda_{max.}$ 230 (ε 18 500) and 290 nm (5 270), unchanged on the addition of one drop of 70% perchloric acid; m/z 455 (M^+, 100%), 424 (40), 396 (82), and 336 (92); δ 7.38—6.60 (4 H, m, aryl H), 6.10 (1 H, s, olefinic H), 3.74 (6 H, s, 2 OMe), 3.70 (3 H, s, OMe), 3.40 and 3.43 (2 H, CH$_2$), 2.69 (3 H, s, NMe), and 2.56—1.40 (6 H, m, aliphatic H) (unchanged after shaking with D$_2$O).

The addition of *ca.* 0.3 mol. equiv. of Eu(fod)$_3$ to D, in CCl$_4$–CHCl$_3$, caused the two singlets at δ 3.40 and 3.43 to shift to δ 6.00 (1 H, d, J 17 Hz) and 6.28 (1 H, d, J 17 Hz), respectively.

(iii) The brown band (R_f 0.1) yielded yellow needles (from ethanol) (50 mg) of the *adduct* (10), m.p. 164—165° (Found: C, 68.0; H, 5.9; N, 4.7. $C_{17}H_{17}NO_4$ requires C, 68.2; H, 5.8; N, 4.7%); $\nu_{max.}$ 3 100—2 500m, 1 750infl, 1 725s, and 1 670—1 635m cm^{-1}; $\lambda_{max.}$ 232 (ε 13 160) and 290 nm (1 500), unchanged on the addition of one drop of 70% perchloric acid; m/z 299 (M^+, 100%), 255 (45), 214 (30), 210 (40), and 185 (30); δ 12.1 (1 H, br s, CO$_2$H, disappeared on shaking with D$_2$O), 7.45—6.70 (4 H, m, aryl H), 6.61 (1 H, s, olefinic H), 3.04 (3 H, s, NMe), and 3.40—1.00 (8 H, m, aliphatic H). Treatment with an excess of ethereal diazomethane resulted in a rapid and vigorous reaction. After 30 s, excess of acetic acid was added and the solution evaporated yielding the *adduct* (9) quantitatively, as pale yellow prisms (from ethanol), m.p. 152—153° (Found: C, 69.3; H, 6.3; N, 4.5. $C_{18}H_{19}NO_4$ requires C, 69.0; H, 6.1; N, 4.5%), $\nu_{max.}$ 1 755s, 1 735s, 1 675w, and 1 610w cm^{-1}; $\lambda_{max.}$ 233 (ε 14 000), and 285 nm (1 500); m/z 313 (M^+, 100%), 210 (50), and 113 (40); δ 7.30—6.50 (4 H, m, aryl H), 6.42 (1 H, s, olefinic H), 3.84 (3 H, s, OMe), 2.97 (3 H, s, NMe), and 2.70—1.10 (8 H, m, aliphatic H).

(*b*) The carbazole (4) (1 g) and DMAD (2 g) were refluxed in methanol (40 ml) containing 3% of water for 8 days. Evaporation under reduced pressure and p.l.c. (chloroform) yielded numerous bands [viewed under u.v. light (254 nm)]; crystalline material was obtained from two of these.

(i) The orange/yellow band (R_f 0.6) gave yellow plates (from ethanol) (0.2 g), m.p. 110—135° which on repeated p.l.c. (1% ethyl acetate in chloroform) separated into two bands, one very pale yellow (R_f 0.6) and the other bright yellow (R_f 0.7). The R_f 0.7 band yielded yellow needles (from ethanol) of the *adduct* (8) (75 mg), m.p. 111—113° (Found: C, 68.9; H, 6.3; N, 4.4. $C_{18}H_{19}NO_4$ requires C, 69.0; H, 6.1; N, 4.5%), $\nu_{max.}$ 1 752s, 1 724s, 1 665w, and

1 600w cm^{-1}; $\lambda_{max.}$ 237 (ε 13 000) and 275 nm (1 400), unchanged on addition of one drop of 70% perchloric acid; m/z 313 (M^+, 100%), 279 (60), 210 (82), 167 (75), and 157 (20); δ 7.6 (1 H, dd, J 7 and 1.5 Hz), 7.2 (1 H, dt, J 7 and 1.5 Hz), 6.8 (1 H, dt, J 7 and 1.5 Hz), 6.58 (1 H, d, J 7 Hz), 6.98 (1 H, s, olefinic H), 3.88 (3 H, s, OMe), 2.95 (3 H, s, NMe), and 2.9—1.1 (8 H, m, aliphatic H) (unchanged after shaking with D$_2$O). The R_f 0.6 band yielded pale yellow plates (from ethanol) of the *adduct* (12) (75 mg), m.p. 155—156° (Found: C, 68.9; H, 6.4; N, 4.5. $C_{18}H_{19}NO_4$ requires C, 69.0; H, 6.1; N, 4.5%); $\nu_{max.}$ 1 715br, s cm^{-1}; $\lambda_{max.}$ 235 (ε 12 600) and 290 nm (4 200), unchanged on the addition of one drop of 70% perchloric acid; m/z 313 (43%), 269 (14), 254 (14), 241 (15), 240 (15), 228 (20), 210 (30), 185 (100), and 157 (60); δ 7.42 (1 H, dd, J 7 and 1.5 Hz), 7.20 (1 H, dt, J 7 and 1.5 Hz), 6.82 (1 H, dt, J 7 and 1.5 Hz), 6.65 (1 H, s, olefin H), 6.58 (1 H, d, J 7 Hz), 3.81 (3 H, s, OMe), 2.84 (3 H, s, NMe), and 2.3—0.7 (8 H, m, aliphatic H), unchanged after shaking with D$_2$O.

(ii) The pale yellow band (R_f 0.2) gave colourless plates (0.45 g), m.p. 129—130°, unchanged on mixing with compound D.

5-Methyl-5,6,7,8,9,10-hexahydrocyclohept[b]*indole* (5).—Phenylhydrazine and cycloheptanone, by the method of Perkin,[14] gave 5,6,7,8,9,10-hexahydrocyclohept[b]indole (from ethanol) m.p. 144—145° (lit.,[14] 144°) in 70% yield. Methylation with sodium hydride and dimethyl sulphate gave the indole (5), m.p. 50—51° (lit.,[15] 50°) in 80% yield.

The Indole (5) *with Dimethyl Acetylenedicarboxylate.*—The indole (5) (1.2 g) and DMAD (3 g) were refluxed in wet methanol (30 ml) for 1 week. Evaporation and p.l.c. (chloroform) afforded no starting material (5) (R_f 0.9) but gave numerous coloured bands, from which crystalline material was obtained in only one case.

The pale yellow band (R_f 0.3) which appeared dark under u.v. light (254 nm) gave colourless crystals (from ethanol) of compound F, m.p. 156—157° (Found: C, 63.9; H, 5.7; N, 2.9. Calc. for $C_{25}H_{27}NO_8$: C, 64.0; H, 5.8; N, 3.0%); $\nu_{max.}$ 1 765s, 1 735infl, 1 720s, 1 630w, and 1 605 cm^{-1}; $\lambda_{max.}$ 246 (ε 15 100), and 304 nm (4 200); m/z 469 (M^+, 65%), 438 (15), 410 (100), and 350 (90); δ 7.35—6.32 (4 H, m, aryl H), 6.58 (1 H, s, olefinic H), 3.73, 3.68, and 3.17 (9 H, each s, 3 $\times$ OMe), 3.45 (2 H, s, CH$_2$), 2.70 (3 H, s, NMe), and 3.0—0.8 (8 H, m, aliphatic H) unchanged on shaking with D$_2$O. The addition of 0.02 mmol of Eu(fod)$_3$ to 0.1 mmol of compound F in hexadeuteriobenzene caused one of the methoxy-signals (δ 3.35), the methylene signal (δ 3.35), and the olefinic H signal (δ 6.57) to shift to δ 5.5, 7.05, and 8.3, respectively, with all the signals remaining as clearly defined singlets.

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