Addition Reactions of Heterocyclic Compounds. Part 79.[1] Reaction of Dimethyl Acetylenedicarboxylate with some Cyclohept[*b*]indoles and Cyclo-oct[*b*]indoles

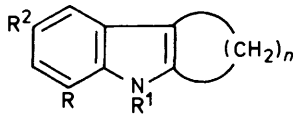
Roy M. Letcher * and Michael C. K. Choi
Department of Chemistry, University of Hong Kong, Hong Kong
R. Morrin Acheson
Department of Biochemistry, South Parks Road, Oxford OX1 3QU

The reactions of dimethyl acetylenedicarboxylate with *N*-methyl- and pyrido[3,2,1-*hi*]indoles which have either a penta- or hexa-methylene chain linking positions 2 and 3, have been found to give rise to a very similar array of products. Nineteen new adducts were isolated and their structures established by ^{1}H and ^{13}C n.m.r. spectral comparisons, and in some cases also by chemical transformations. The structures include five new classes of adducts not previously encountered: two types of (1 + 1 DMAD) adducts, one of which is a cyclobutene and the other a 3-maleate; two types of (1 + 2 DMAD) adducts, one with two side chains, and the other having a ring-expanded nine- or ten-membered ring and one side chain; and a (1 + 2 DMAD − CH_4O) adduct, all examples of which exhibit fragmentation on heating to give a carbazole and a spiro-cycloalkyl-keten dimer. The isolation of the two (1 + 1 DMAD) adducts is important as both adduct types have been postulated as intermediates in the formation of more complex adducts.

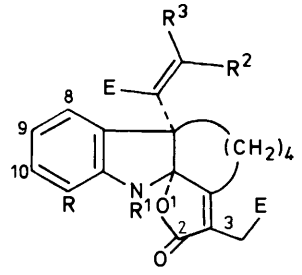
Addition of dimethyl acetylenedicarboxylate (DMAD) to indoles is invariably initiated by electrophilic attack at the 3-position. Thus, indole gives a maleate, a fumarate, and through further cyclisation and ring opening, a benzazepine [2] which can react further.[3] 2,3-Dialkylindoles cyclise to give dienones even when the 2,3-positions are linked by a deca-methylene chain.[4] In the case of *N*-methyl- and pyrido-[3,2,1-*hi*]-indoles with a tri- or tetra-methylene chain joining the 2- and 3-position and thus preventing dienone formation, the products are mainly lactones of various types,[1,5] but also include some products unique to each ring system, *e.g.* only the carbazole (1) gives lactones with an extra ring formed by a new C–C bond linking a DMAD moiety to the normally unreactive CH_2N function; [1] the cyclopentenes [*e.g.* (2)] undergo ring opening after reacting with DMAD and water to give an oxo-benzazocine.[1]

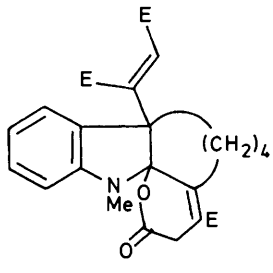
It was therefore of interest to find what effect a penta- or hexa-methylene chain joining positions 2 and 3, would have on reactions of DMAD with *N*-methyl- and pyrido[3,2,1-*hi*]-indoles. To this end we have already isolated the lactone (9),[3] the sole product from indole (3) and DMAD in wet methanol. We now report our investigations of the addition of DMAD to indoles (4), (5), and (6), and further reactions of (3), in acetic acid, methanol, and acetonitrile.

First, the reactions of the indoles with a penta-methylene chain are as follows. Indole (3) in wet acetic acid gave two products: colourless A and orange B. Compound A, a (1 + 2 DMAD − CH_2) adduct gives spectra (see Table 1 for ^{13}C n.m.r. data) almost identical with that of the previously described adduct F from (3) [5] except that the bis(methoxy-carbonyl)vinyl side-chain in A has the (*Z*)-configuration (the ester CO at δ 167.3 is coupled to the olefinic proton with *J* 11.9 Hz).[6] Following the same argument used previously,[5] A must be either compound (10) or (13). We have now obtained the *X*-ray crystal structure of adduct F and found it to be (9),[7] which strongly suggests that A is its geometrical isomer (10). Mass spectrometry should enable a distinction to be made between such structures as (10) and (13), since only (13) would be expected to show a fragment ion for the loss of CO_2 as a result of a retro-Diels–Alder process. Since neither A nor (9) exhibit such an ion in their mass spectra, this further confirms the structure of A as (10). Compound B is formed by the addition of two moles of DMAD to the indole (3) and the loss of 'CH_4O'. All spectra (see Table 2 for ^{13}C n.m.r. data) are highly reminiscent of the analogous (1 + 2 DMAD − CH_4O) adduct obtained from indole (7), whose structure has been established as (14) by *X*-ray crystallography.[8] Furthermore, both compounds (14) and B give analogous products on degradation (see later), which further confirms the structure of B as the spiro-compound (15). This structure (15) strongly suggests that it is formed from the carbazole-spirocyclo-



(1) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 4
(2) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 3
(3) R = R^2 = H, R^1 = Me, *n* = 5
(4) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 5
(5) R = R^2 = H, R^1 = Me, *n* = 6
(6) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 6
(7) R = H, R^1 = Me, R^2 = Br, *n* = 5
(8) R = R^1 = R^2 = H, *n* = 6





(9) R = R^3 = H, R^1 = Me, R^2 = E
(10) R = R^2 = H, R^1 = Me, R^3 = E
(11) R, R^1 = $(CH_2)_3$, R^2 = H, R^3 = E
(12) R, R^1 = $(CH_2)_3$, R^2 = E, R^3 = H

(13)

E = CO_2Me

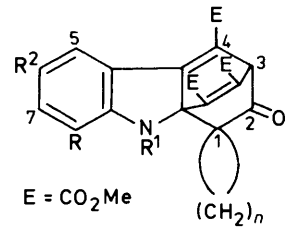
Table 1. ^{13}C N.m.r. spectra of the (1 + 2 DMAD − CH_2) lactones for solutions in $CDCl_3$ measured at 22.63 MHz and recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

	Compounds		
	A		
Assignments	(10)	(11)	(12)
Lactone CO	169.9s [a]	170.3s [e]	171.3s [i]
Ester CO	169.2s [b]	169.5s [f]	169.7s [j]
	167.3s [c]	167.7s [g]	167.9s [k]
	164.9s [d]	165.3s [h]	165.4s [l]
sp^2-C	162.3s	162.4s	162.4s
	150.6s	150.7s	146.2s
	149.0s	145.5s	142.5s
	128.0s	126.2s	126.0s
	124.4s	122.4s	124.7s
		118.4s	116.6s
sp^2-CH	129.3d	128.1d	128.9d
	125.1d	125.1d	127.9d
	123.8d	124.0d	122.5d
	118.4d	118.2d	117.1d
	105.8d		
sp^3-C-N(-O)	108.7s	108.9s	108.7s
sp^3-C	59.4s	61.0s	59.5s
OMe	51.9q	52.2q	52.3q
	51.9q	52.2q	52.3q
	51.4q	51.7q	51.6q
NMe	26.4q		
sp^3-CH_2	35.9t	38.6t	38.7t
	28.4t	36.2t	36.5t
	26.2t	28.7t	28.8t
	26.2t	26.7t	27.0t
	23.1t	26.7t	26.8t
		24.3t	24.4t
		23.4t	23.8t
		22.0t	22.1t

Coupling constants (Hz) from proton-coupled spectra.

[a] t, J_{CO,CH_2} 4.9. [b] m. [c] dq, $J_{CO,H}$ 11.9; $J_{CO,Me}$ 3.9. [d] dq, $J_{CO,H}$ 1.6; $J_{CO,Me}$ 3.8. [e] t, $J_{CO,Me}$ 3.7. [f] m. [g] dq, $J_{CO,H}$ 11.7; $J_{CO,Me}$ 4.0. [h] dq, $J_{CO,H}$ 1.5; $J_{CO,Me}$ 4.0. [i] t, J_{CO,CH_2} 4.7. [j] m. [k] dq, $J_{CO,H}$ 8.0; $J_{CO,Me}$ 3.8. [l] dq, $J_{CO,H}$ 1.5; $J_{CO,Me}$ 4.1.

pentane (21) (see Scheme 1) by a Diels–Alder reaction across the 3,9a-positions as indicated. On this assumption and that DMAD attacks the initial indole yielding (22), then the polymethylene chain must break away from the 3-position and attach itself at the 1-carbon atom of structure (21). This may be rationalised in several ways, two of which begin with the formation of the enamine (23) [the existence of which is now substantiated as a result of the isolation of enamine (40), see later]. Nucleophilic attack by the enamine at one ester would give the cation (24), a process with numerous analogies.[4] Loss of the 1-proton could not give an sp^2-C atom at this position because of strain, so a concerted loss of this proton and a 1,3-shift of the tetramethylene bridge would be needed to give compound (21). An alternative 1,2-shift, well known in the indole series, could give the cation (25) where the positive charge could be delocalised into the nitrogen atom [*cf.* (26)]. Loss of a proton from position-1, with perhaps the formation of the tautomer (26), followed by another 1,2-shift



(14) R = H, R^1 = Me, R^2 = Br, *n* = 4
(15) R = R^2 = H, R^1 = Me, *n* = 4
(16) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 4
(17) R = R^2 = H, R^1 = Me, *n* = 5
(18) R, R^1 = $(CH_2)_3$, R^2 = H, *n* = 5
(19) R = R^1 = R^2 = H, *n* = 4
(20) R = R^1 = R^2 = H, *n* = 5

could also yield (21). One other possibility envisages nucleophilic attack by solvent at a methylene carbon of (22) leading to a spiro-enamine and ultimately to the spiro-compound (21), as shown in Scheme 1. However, we have found that the maleate (40), an isomeric analogue of (23), is stable in refluxing acetic acid, and does not even undergo geometrical isomerism. In wet acetonitrile, the indole (3) with DMAD gave the isomeric compounds, yellow C and orange D (both of which were formed by the addition of two moles of DMAD to the indole), together with a red compound E. Adducts C and D give fairly similar spectra (including ^{13}C n.m.r. multiplicities, see Table 3), both having four ester groups and two olefinic protons, but important differences can be seen. The ^1H n.m.r. spectrum of compound C shows one olefinic proton as a singlet and the other as a double doublet (*J* 5, 12 Hz), and the proton-coupled ^{13}C n.m.r. spectrum shows that each olefinic proton is strongly coupled to an ester CO (*J* 12.6 and 10.6 Hz), one ester CO is weakly coupled (*J* 0.9 Hz), and the remaining ester CO is not coupled to either olefinic proton. Consequently, two of the ester groups must have a *trans*-relationship [6] with the olefinic protons, and assuming that the reaction occurs by known pathways [3,5,9] (see Scheme 2) the likely structure appears to be (27). Compound D on the other hand has a ^1H n.m.r. spectrum showing both olefinic protons as singlets, and in the proton-coupled ^{13}C n.m.r. spectrum (see Table 3) each is strongly coupled to an ester CO group (*J* 12.3 and 12.0 Hz), and also weakly coupled (*J* 2.1 and 1.4 Hz) to the remaining two ester CO groups. The most likely structure for D is therefore (31) which has two maleate side chains and may also be considered to be formed *via* known pathways (Scheme 2). Compound E is formed by the addition of one mole of DMAD to the indole, and in its ^{13}C n.m.r. spectrum shows two sp^3 and four sp^2 carbon atoms not bonded to hydrogen (Table 4). This indicates structure (35) for compound E, the cyclobutene ring being in agreement with the mass spectrum which shows the apparent loss of DMAD to give an ion corresponding to the molecular ion of the parent indole (3). The usual ring-opening to a benzazepine [2] cannot occur in this case because of the steric strain produced by the relatively short polymethylene chain. The isolation of compound (35) appears to be the first instance of a cyclobutene being isolated from DMAD and an indole, although one has been obtained [10] from 1-acetyl-3-*N*-piperidinoindole and methyl propiolate, where the 3-substituent controls the mode of addition and isomerisation to the corresponding benzazepine easily occurs. The formation of (35) (and its analogues) in a protic solvent shows that the normally favoured [2] quenching of an intermediate zwitterion, such as (39) (in Scheme 2), by the solvent need not occur exclusively.

Table 2. ^{13}C N.m.r. spectra of (1 + 2 DMAD − CH_4O) adducts 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

	Compounds						
		B					
Assignments	(14)	(15)	(16)	(17)	(18)	(19)	(20)
Ketone CO	205.8s	206.6s	206.7s	202.3s	202.4s	206.1s	202.7s
Ester CO	166.2s	166.5s	166.6s [a]	166.5s	166.5s	165.7s	165.6s
	163.9s	164.3s	164.4s [b]	164.3s	164.4s	164.2s	164.2s
	162.7s	162.8s	162.8s [c]	162.9s	162.9s	163.9s	163.9s
sp^2-C	156.9s	158.5s	159.0s	158.2s	158.7s	158.9s	158.1s
	156.4s	157.6s	154.7s	157.5s	154.4s	157.3s	156.9s
	149.0s	149.4s	149.8s	148.0s	148.6s	144.9s	143.8s
	128.2s	128.1s	128.0s	128.0s	127.8s	132.2s	132.0s
	121.1s	119.3s	118.8s	119.3s	118.7s	120.8s	120.7s
	115.0s	113.3s	117.6s	113.1s	117.6s	113.8s	113.5s
	110.1s		112.8s		112.5s		
sp^2-CH	136.7d	134.3d	132.6d	134.3d	132.5d	134.1d	134.0d
	131.3d	128.9d	126.7d	128.8d	126.4d	129.1d	128.9d
	107.9d	118.2d	117.9d	118.2d	117.8d	119.7d	119.6d
		106.5d		106.5d		110.4d	110.4d
sp^3-C	82.5s	82.2s	82.2s	84.3s	84.2s	78.7s	79.9s
	50.3s	50.5s	50.1s	44.3s	43.5s	50.8s	53.1s
sp^3-CH	56.3d	56.1d	56.0d	57.5d	57.4d	58.1d	59.0d
OMe	53.0q	53.0q	52.9q	53.0q	52.7q	52.8q	52.7q
	52.8q	52.8q	52.8q	52.8q	52.7q	52.8q	52.7q
	52.2q	52.0q	52.0q	52.0q	51.8q	52.0q	52.0q
NMe	31.0q	30.8q		32.4q			
sp^3-CH_2	36.3t	36.9t	43.2t	32.8t	45.0t	36.5t	43.0t
	34.3t	34.2t	36.5t	30.3t	32.7t	34.1t	32.7t
	27.5t	27.5t	33.9t	25.4t	30.2t	27.6t	29.6t
	27.4t	27.4t	27.4t	21.9t	25.4t	27.5t	25.0t
			27.3t	21.2t	24.7t		21.9t
			24.7t		22.7t		
			22.6t		22.0t		
					21.0t		

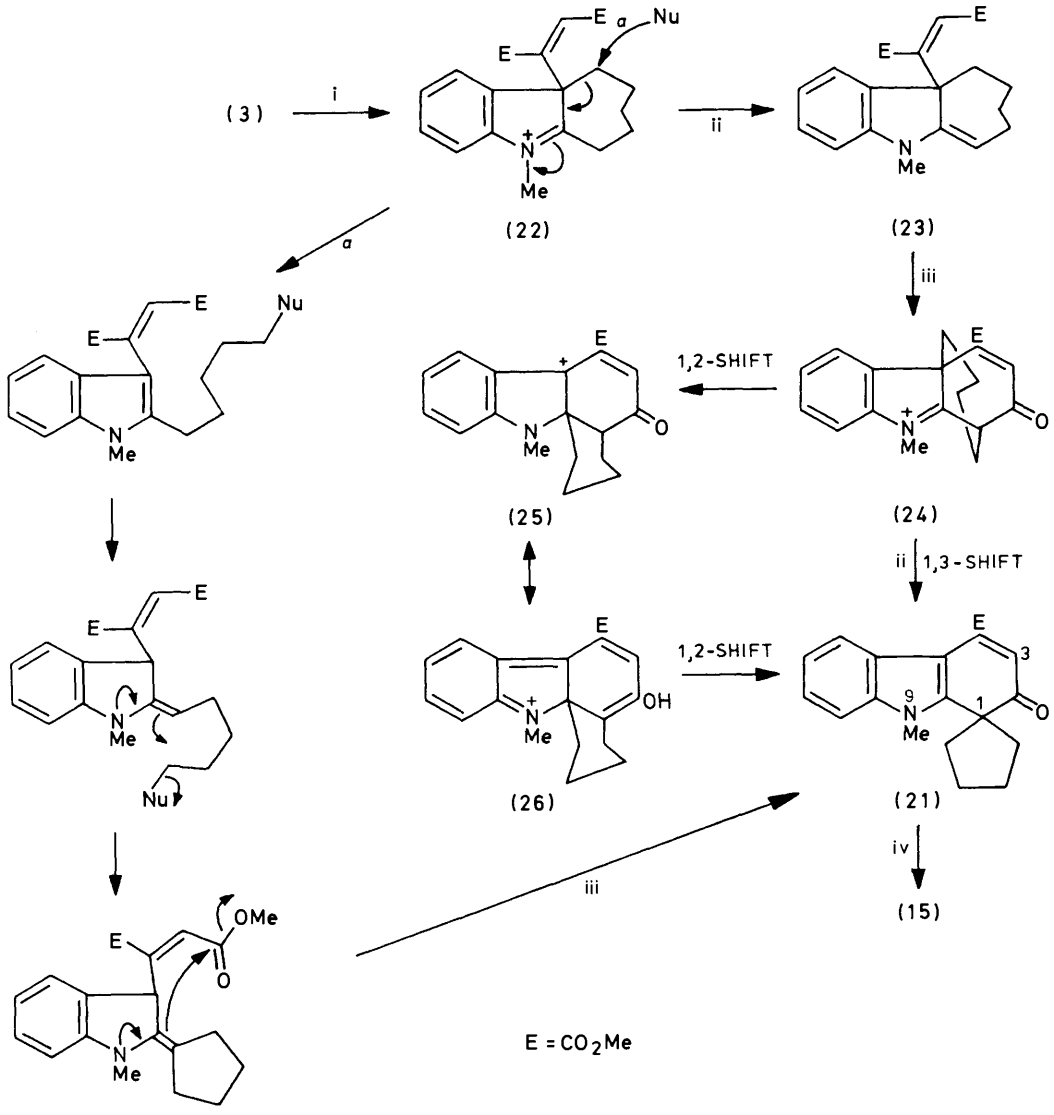
Coupling constants (Hz) from proton-coupled spectra.

[a] dq, $J_{CO,H}$ 1.0; $J_{CO,Me}$ 3.9. [b] dq, $J_{CO,H}$ 3.9; $J_{CO,Me}$ 3.9. [c] dq, $J_{CO,H}$ 3.2; $J_{CO,Me}$ 4.0.

In either wet methanol or acetic acid, the cycloheptene (4) with DMAD gave the colourless lactone (11), the orange spiro-compound (16), and the red cyclobutene (36), all identified by spectral comparisons (see Tables 1, 2, and 4, respectively). On standing in chloroform over alumina, compound (11) isomerised to (12), identified from the spectral changes (see Table 1). In wet acetonitrile the reaction of the indole (4) with DMAD gave compounds (28), identified from spectral comparisons (see Table 3 for ^{13}C n.m.r. data), and (36) both in good yield.

The addition of DMAD to indoles with a hexamethylene chain joining positions-2 and -3, which has not previously been reported, was carried out first with (5). From the reaction in wet methanol at ambient temperature, (5) and DMAD gave products (29), (32), and (33), their structures following from spectral comparisons (see Table 3 for ^{13}C n.m.r. data). On refluxing the same mixture, only compounds (32) and (29) were formed. In wet acetonitrile, products (29), (32), and (37) (see Table 4) were isolated, all in good yield. In wet acetic acid at room temperature the reaction of the indole (5) with DMAD gave a pale yellow adduct (40) as the major product, together with small yields of compounds (17) (see Table 2), (29), and (32). When the reaction temperature was raised to 80 °C, (17) was the major product, with small amounts of compounds (40), (29), and (32) being isolated. On refluxing the mixture, only products (17) and (42) (see later) were isolated. Compound (40), formed by the addition of one mole of DMAD to the indole, is isomeric with (37) but quite different from it; apart from being different in colour, it exhibits two olefinic protons. This together with the ^{13}C n.m.r. spectra data (see Table 4) is consistent only with the structure (40). This isolation of the cyclo-octa-indole (40) has enabled us to check our proposed mechanism for the formation of the (1 + 2 DMAD) adducts [*e.g.* (29) and (32)] as detailed in Scheme 2, since the (1 + 1 DMAD) adduct (40) is actually the first intermediate product in the series of hypothetical reactions leading to compounds (29) and (32). Treatment of (40) with DMAD in acetic acid did in fact yield products (29) and (32), only. Consequently, this result strongly supports our proposed mechanism, as well as the structures of the (1 + 2 DMAD) adducts (27)—(34).

Addition of DMAD to the indole (6) in either wet methanol or wet acetic acid gave four adducts, (18), (30), (34), and (38), all identified from spectral comparisons (see Tables 2, 3, and 4). When this reaction was carried out in deuteriated acetic



Scheme 1. *Reagents:* i, EC≡CE, H^+; ii, $-H^+$; iii, $-MeOH$; iv, EC≡CE

acid–deuterium oxide, only the olefinic protons were found to be absent from the ^1H n.m.r. spectra of the subsequently isolated products (30) and (34), an observation which is not inconsistent with their structures, and which suggests that the enaminic proton in (40) also exchanges. In wet acetonitrile the indole (6) gave compounds (30), (34), and (38). The olefinic protons of (30) and (34) were again absent when water was replaced by deuterium oxide in the synthesis.

The four orange (1 + 2 DMAD − CH_4O) adducts (15)—(18) all undergo similar degradation reactions to that shown by the analogous bromo-adduct (14).[8] Firstly, all exhibit similar mass spectra with a low intensity molecular ion, and a base peak formed by the loss of either 110 a.m.u. [in the case of the adducts (17) and (18), obtained from indoles with an 8-membered ring] or 96 a.m.u. [from adducts (14), (15), and (16) which are all obtained from indoles with a 7-membered ring], which is not accompanied by a metastable peak. In the case of spiro-compounds (15) and (16), the base peaks have been identified as ($C_{19}H_{17}NO_6^+$) and ($C_{21}H_{19}NO_6^+$) respectively, by high resolution mass spectrometry. This same fragmentation apparently also occurs on heating since at *ca.* 200 °C each of the (1 + 2 DMAD − CH_4O) adducts yields a residue identified as a 1,2,4-tris(methoxycarbonyl)carbazole, which in each case appears to be the actual compound responsible for the base peak in the mass spectra, and suggests that the base peak is formed *via* thermal decomposition. Mass spectra of these involatile adducts is only possible when the sample probe is heated to within 10—20 °C of their m.p.s. The structure of each carbazole follows from analytical and spectral data, including the ^{13}C n.m.r. spectra (Table 5), and also from an interpretation of the most likely mechanism of fragmentation, which is shown in Scheme 3 as a retro-Diels–Alder process. The thermolysis reaction also yielded in each case a second product which could be distilled, and which was identified as a cycloalkyl-keten dimer in each case, from analytical and spectral data (see Table 5 for the ^{13}C n.m.r. data). Thus adduct (15) gives products (42) and (47); adduct (16) gives (43) and (47); adduct (17) gives (42) and (48); adduct (18) gives (43) and (48); and adduct (14) gives (41) and (47) (see Scheme 3). The fragmentation process was also found to be initiated by attack of hydride ion, as each (1 + 2 DMAD − CH_4O) adduct gives the same carbazole on treatment with $NaBH_4$ as that obtained from thermolysis. Carbazole (42) has been reported earlier [11] but its structure

Table 3. ^{13}C N.m.r. spectra of (1 + 2 DMAD) adducts for solutions in $CDCl_3$ measured at 22.63 MHz and recorded as δ value (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

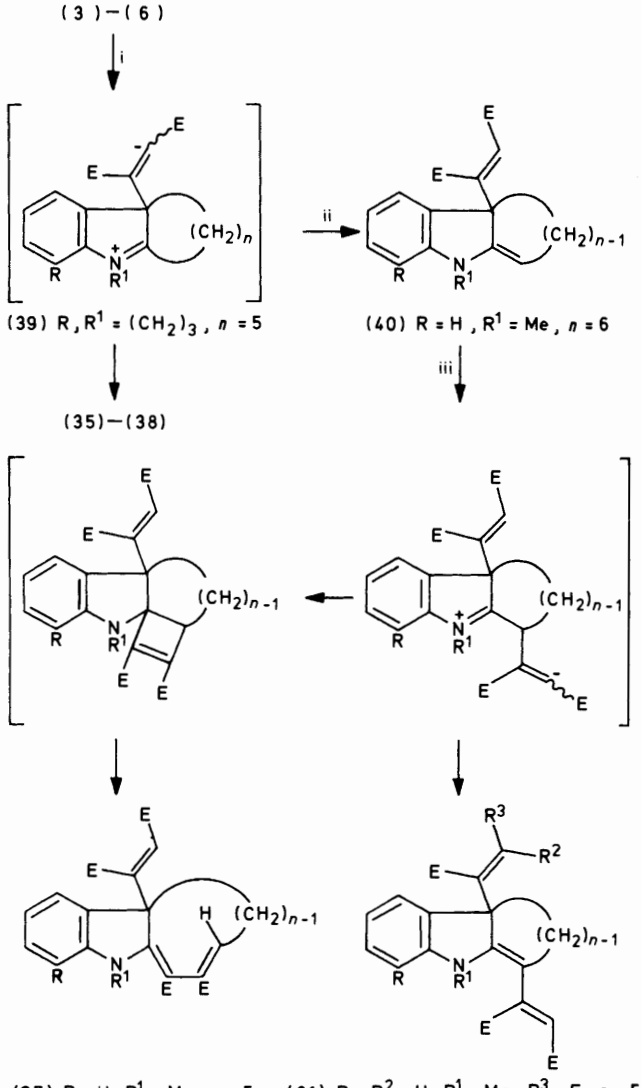
	Compounds							
	C				D			
Assignments	(27)	(28)	(29)	(30)	(31)	(32)	(33)	(34)
Ester CO	167.5s [a]	167.9s [e]	167.1s [i]	167.6s [m]	168.6s [q]	168.8s [u]	169.1s [y]	168.8s [α]
	167.4s [b]	167.6s [f]	166.7s [j]	167.2s [n]	167.1s [r]	166.7s [v]	167.9s [z]	166.7s [β]
	166.2s [c]	166.0s [g]	165.8s [k]	166.0s [o]	166.4s [s]	166.4s [w]	166.6s [•]	166.3s [γ]
	165.8s [d]	166.0s [h]	165.3s [l]	165.9s [p]	165.2s [t]	165.2s [x]	165.7s [k]	165.2s [δ]
sp^2-C	166.2s	164.9s			154.7s	153.1s	157.2s	151.3s
	147.7s	147.6s	163.7s	163.0s	150.3s	151.3s	150.5s	149.5s
	144.4s	139.7s	152.9s	153.0s	149.7s	150.3s	147.4s	142.1s
		134.4s	145.3s	140.7s	147.8s	147.3s	145.5s	133.4s
	136.2s		131.8s	130.7s	133.9s	135.4s	137.2s	120.1s
	129.4s	129.9s	125.2s	125.8s				118.3s
		121.6s		127.0s	107.6s	104.0s	100.0s	101.2s
	101.7s	100.4s	99.6s	98.6s				
sp^2-CH	153.6d	153.0d	153.9d	154.1d	129.0d	128.8d	128.1d	127.0d
	128.6d				122.7d			
	126.6d	127.1d	128.5d	127.2d	120.5d	122.2d	125.8d	119.9d
	124.3d	126.3d	122.8d	121.7d	120.2d	120.5d	122.6d	119.7d
	122.2d	122.4d	121.9d	121.2d	117.2d	118.9d	120.4d	118.3d
	108.8d	121.8d	119.5d	119.9d	107.4d	117.0d	116.0d	116.5d
			108.9d			107.6d	107.2d	
sp^3-C	61.9s	62.9s	61.1s	62.5s	58.3s	57.6s	57.0s	58.3s
OMe	52.2q	52.2q	51.8q	52.2q	52.5s	52.3q	52.7q	52.3q
	51.5q	51.7q	51.3q	51.6q	52.3q	52.2q	52.2q	52.1q
	51.2q	51.4q	50.8q	51.6q	52.0q	52.0q	52.0q	52.0q
	51.1q	51.2q	50.7q	51.6q	51.7q	51.7q	51.5q	51.7q
NMe	37.1q		36.4q		37.4q	38.1q	38.0q	
sp^3-CH_2	41.2t	48.1t	33.4t	47.8t	34.7t	42.1t	43.1t	48.8t
	31.1t	41.1t	29.8t	33.7t	29.0t	28.9t	29.2t	41.8t
	29.6t	31.1t	27.7t	30.2t	27.8t	28.1t	26.8t	28.6t
	23.0t	29.6t	26.8t	28.1t	27.4t	25.1t	25.6t	28.0t
		24.5t	21.9t	27.2t		23.4t	24.1t	25.2t
		23.0t		24.3t				24.6t
		22.3t		22.5t				23.2t
				22.3t				22.8t

Coupling constants (Hz) from proton-coupled spectra.

[a] dq, $^3J_{CO,H}$ 12.6; $^3J_{CO,CH_3}$ 4.0. [b] dq, $^3J_{CO,H}$ 10.6; $^3J_{CO,CH_3}$ 4.0. [c] q, $^3J_{CO,CH_3}$ 3.7. [d] dq, $^2J_{CO,H}$ 0.9; $^3J_{CO,CH_3}$ 3.9. [e] dq, $^3J_{CO,H}$ 13.0; $^3J_{CO,CH_3}$ 3.9. [f] dq, $^3J_{CO,H}$ 11.8; $^3J_{CO,CH_3}$ 3.9. [g] Signal obscured. [h] dq, $^2J_{CO,H}$ 1.1; $^3J_{CO,CH_3}$ 3.9. [i] dq, $^3J_{CO,H}$ 11.8; $^3J_{CO,CH_3}$ 4.0. [j] dq, $^3J_{CO,H}$ 12.3; $^3J_{CO,CH_3}$ 4.0. [k] q, $^3J_{CO,CH_3}$ 3.9. [l] dq, $^2J_{CO,H}$ 1.0; $^3J_{CO,CH_3}$ 3.9. [m] dq, $^3J_{CO,H}$ 11.4; $^3J_{CO,CH_3}$ 4.2. [n] dq, $^3J_{CO,H}$ 10.2; $^3J_{CO,CH_3}$ 4.3. [o] q, $^3J_{CO,CH_3}$ 3.5. [p] dq, $^2J_{CO,H}$ 1.0; $^3J_{CO,CH_3}$ 3.5. [q] dq, $^3J_{CO,H}$ 12.0; $^3J_{CO,CH_3}$ 3.9. [r] dq, $^3J_{CO,H}$ 12.3; $^3J_{CO,CH_3}$ 4.0. [s] dq, $^2J_{CO,H}$ 2.1; $^3J_{CO,CH_3}$ 4.1. [t] dq, $^2J_{CO,H}$ 1.4; $^3J_{CO,CH_3}$ 3.9. [u] dq, $^3J_{CO,H}$ 11.6; $^3J_{CO,CH_3}$ 3.8. [v] dq, $^3J_{CO,H}$ 11.8; $^3J_{CO,CH_3}$ 4.1. [w] dq, $^2J_{CO,H}$ 2.1; $^3J_{CO,CH_3}$ 3.9. [x] dq, $^2J_{CO,H}$ 1.0; $^3J_{CO,CH_3}$ 4.0. [y] dq, $^3J_{CO,H}$ 11.9; $^3J_{CO,CH_3}$ 3.9. [z] dq, $^3J_{CO,H}$ 8.1; $^3J_{CO,CH_3}$ 4.0. [•] dq, $^2J_{CO,H}$ 2.25; $^3J_{CO,CH_3}$ 3.9. [α] dq, $^3J_{CO,H}$ 10.3; $^3J_{CO,CH_3}$ 4.0. [β] dq, $^3J_{CO,H}$ 12.0; $^3J_{CO,CH_3}$ 4.1. [γ] dq, $^2J_{CO,H}$ 0.8; $^3J_{CO,CH_3}$ 3.4. [δ] dq, $^2J_{CO,H}$ 1.0; $^3J_{CO,CH_3}$ 3.9.

had not been fully confirmed. As the carbazole isolated from compounds (15) and (17) is identical with that obtained earlier,[11] this constitutes a formal structural proof of carbazole (42).

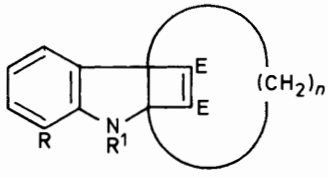
The *N*-methyl-(1 + 2 DMAD − CH_4O) adducts (15) and (17) also exhibit some unusual reactions not shown by the pyrido-carbazoles (16) and (18). Although isolated from reactions carried out in acetic acid (at or below 100 °C), (15) and (17) react in the boiling solvent to give, in good yield, compounds (19) and (42), respectively. The structure of (19) followed from spectral data (see Table 2 for ^{13}C n.m.r.) and from its conversion into (15) on methylation. This highly specific demethylation of the *N*-methyl-carbazole (15) under the mild conditions of boiling acetic acid, has no analogy as far as we are aware. To account for the reaction we propose a mechanism involving neighbouring-group participation of the ester carbonyl as shown in Scheme 4. Assuming a pyramidal nitrogen in (15), Dreiding models show that the 6-membered transition state, involving the NMe, C-9a, C-10, and the ester CO, is almost planar, with the groups suitably close to one another for demethylation to occur *via* protonation and the stabilised oxonium ion (49). An explanation as to why compound (17) does not exhibit a similar reaction is suggested by models which show that its non-planar spiro-cyclohexane moiety is far more likely to hinder protonation of the nitrogen than the planar cyclopentane ring in (15). The need for acid catalysis of the reactions of the *N*-methyl-carbazoles (15) and (17) is shown by their inert nature in refluxing toluene. Compound (19) behaves in much the same way as its alkyl analogues towards $NaBH_4$, and yields the



Scheme 2. *Reagents:* i, EC≡CE, H^+; ii, $-H^+$; iii, EC≡CE

carbazole (44), but on thermolysis it does not yield any isolable volatile products instead giving a residue formed by the loss of only methanol. From an analysis of the spectral data (see Table 5 for ^{13}C n.m.r.), which show, among other features, the presence of ketone and amide carbonyls, the structure of the residue has been deduced as (50) showing that the cyclopentylketen (45), formed from the thermal fragmentation, is readily trapped by the NH group of the resulting carbazole (see Scheme 3). A similar reaction was shown by the analogous secondary amine (20) which gave compound (51) on heating, but in this case the rearranged product was accompanied by both the keten dimer (48) and the carbazole (44).

From these DMAD addition reactions the following generalisations can be made concerning the type of product obtained from the various indoles: (i) *N*-methyl- and pyrido-[3,2,1-*hi*]-indoles with either a penta- or hexa-methylene chain joining positions 2 and 3, give largely the same type of



adducts, the only real exception being the (1 + 2 DMAD − CH_2) lactones [*e.g.* (10) and (11)] which are formed only by the indoles which have a pentamethylene chain; (ii) furthermore, with the exception of these lactones, all the product types obtained from the indoles with a penta- or hexamethylene chain are quite different from those obtained from the indoles with a tri- or tetra-methylene chain, showing that the type of product formed is largely dictated by the size of the methylene bridge connecting positions 2 and 3 of the indole ring.

No generalised solvent–product dependence could be discerned, though different solvents, temperature, and the amount of water present, do tend to give different products and yields from a particular indole.

Experimental

The instruments and procedures are given in refs. 6 and 9 with the addition that accurate mass determinations were carried out on a VG MM 70-70 mass spectrometer.

Preparation of Indoles.—Reaction of 1-amino-1,2,3,4-tetrahydroquinoline [4] with a ketone followed by hydrolysis gave the following indoles: cycloheptanone gave 5,6,9,10,11,-12-hexahydro-4*H*,8*H*-cyclohepta[4,5]pyrrolo[3,2,1-*ij*]-quinoline (4), m.p. 95—96 °C (lit.,[12] m.p. 96—97 °C), and cyclo-octanone gave white needles of 5,6,8,9,10,11,12,13-*octahydro*-4H-*cyclo-octa*[4,5]*pyrrolo*[3,2,1-ij]*quinoline* (6) (75%), m.p. 48—50 °C (from methanol) (Found: C, 85.4; H, 9.0; N, 6.0. $C_{17}H_{21}N$ requires C, 85.3; H, 8.8; N, 5.9%); $\lambda_{max.}$ 210 infl. (ε 22 000), 232 (30 700), and 286 nm (8 500); *m/z* 239 (M^+, 100%), 210 (65), and 196 (70); δ 7.4—6.7 (3 H, m), 3.9 (2 H, t, *J* 6 Hz), and 3.0—1.0 (16 H, m).

Reaction of cyclo-octanone, with 1-methyl-1-phenylhydrazine, followed by cyclisation with 18% sulphuric acid at 100 °C, gave 5-methyl-6,7,8,9,10,11-hexahydrocyclo-oct[*b*]indole (5), b.p. 135 °C at 0.05 mmHg, picrate, m.p. 76—77 °C (lit.,[13] m.p. 77 °C). Reaction of cyclo-octanone with phenylhydrazine followed by cyclisation with 18% sulphuric acid at 100 °C gave 6,7,8,9,10,11-hexahydro-5*H*-cyclo-oct[*b*]indole (8), m.p. 70—71 °C (lit.,[13] m.p. 71 °C).

Thermolysis Reactions.—All thermolyses were carried out by heating the compound, under reduced pressure (0.1—0.2 mmHg), in an oil bath at 190—210 °C when reaction occurred, and with a cold finger to collect any distillate. After 15 min the residue was crystallised from ethanol, and the oily distillate was redistilled to give a colourless crystalline product.

Sodium Borohydride Reductions.—All $NaBH_4$ reductions were carried out by stirring the compound (200 mg) with $NaBH_4$ (1.0 g) in methanol (80 ml) for 24 h at room temperature, before adding water (5 ml) and evaporating the mixture

Table 4. ^{13}C N.m.r. spectra of (1 + 1 DMAD) adducts 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

	Compounds				
Assignments	E (35)	(36)	(37)	(38)	(40)
Ester CO	161.7s [a]	161.8s [b]	161.8s [c]	161.8s [d]	167.4s [f]
	161.4s [a]	161.5s [b]	161.4s [c]	161.4s [e]	165.5s [g]
sp^2-C	151.3s	147.5s	150.3s	146.5s	152.6s
	144.2s	143.8s	144.2s	143.8s	149.3s
	137.8s	137.3s	137.0s	136.5s	146.7s
	128.0s	125.7s	126.6s	124.5s	134.7s
		118.2s		118.9s	
sp^2-CH	129.1d	127.6d	128.8d	127.3d	128.6d
	124.1d	121.9d	125.1d	122.9d	122.8d
	116.6d	116.2d	116.5d	116.1d	118.9d
	106.2d		106.8d		118.0d
					104.9d
					95.0d
sp^3-C	76.4s	76.3s	75.0s	74.7s	55.2s
	61.7s	62.8s	60.5s	61.5s	
OMe	51.7q	51.7q	51.7q	51.6q	51.8q
	51.7q	51.7q	51.7q	51.6q	51.8q
NMe	30.0q		29.8q		29.3q
sp^3-CH_2		40.7t		41.6t	41.3t
	31.7t	31.8t	27.1t	27.0t	29.4t
	31.0t	31.0t	25.4t	25.4t	25.7t
	30.0t	29.6t	25.4t	$(25.1t)_3$	24.0t
	25.2t	25.3t	25.0t	$(24.9t)_2$	22.9t
	23.6t	25.0t	24.9t	22.5t	
		23.8t	24.8t		
		22.7t			

Coupling constants (Hz) from proton-coupled spectra.

[a] q, $J_{CO,Me}$ 4.0. [b] q, $J_{CO,Me}$ 3.8. [c] q, $J_{CO,Me}$ 4.1. [d] q, $J_{CO,Me}$ 4.1. [e] q, $J_{CO,Me}$ 3.9. [f] dq, $J_{CO,H}$ 10.3; $J_{CO,Me}$ 4.0. [g] dq, $J_{CO,H}$ 2.0; $J_{CO,Me}$ 4.0.

to dryness. Water (25 ml) was added and the pH adjusted to 4 with dilute HCl and the mixture was extracted with chloroform (4 × 25 ml), and p.l.c. (chloroform) carried out.

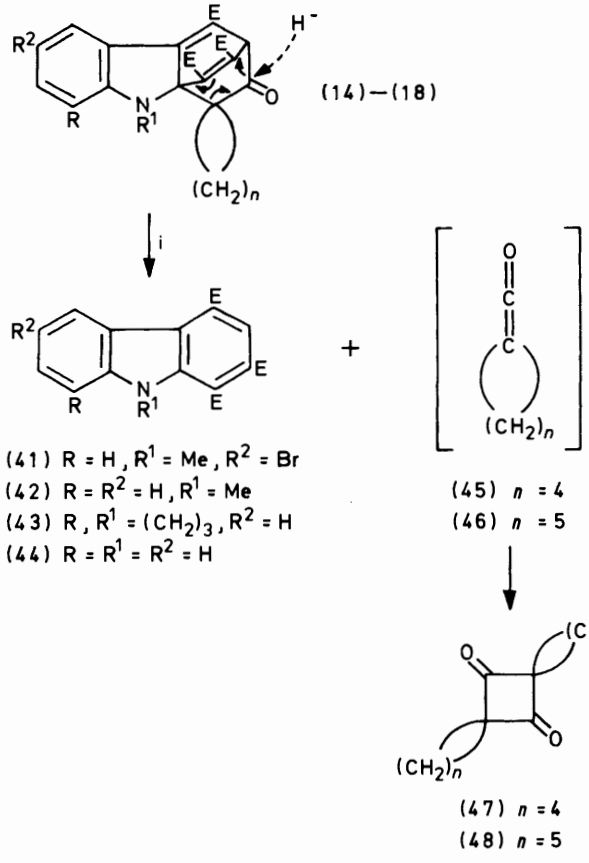
Reaction of the Indole (3) *and Dimethyl Acetylenedicarboxylate.*—(*a*) Reaction of the indole (3) [5] (1 g) and DMAD (2 g) in 98% aqueous acetic acid at 100 °C for 4 days followed by t.l.c. (chloroform) gave two isolable products. (i) The brown band (R_F 0.2) gave colourless rods (0.32 g) (from ethanol) of *dimethyl 3-methoxycarbonylmethyl-12-methyl-2-oxo-4,5,6,7,-7a,12-hexahydro-2H-furo*[2′,3′:2,3]*cyclohepta*[1,2-b]*indol-7a-ylmaleate* (10), m.p. 113—114 °C (Found: C, 63.6; H, 5.8; N, 2.9. $C_{25}H_{27}NO_8$ requires C, 63.95; H, 5.8; N, 3.0%); $\nu_{max.}$ 1 770 infl., and 1728 cm^{-1} (s); $\lambda_{max.}$ 217.5 (ε 23 000), 245 (14 700), and 315 nm (3 300); *m/z* 469 (M^+, 60%), 410 (100), and 351 (88); δ 7.4—6.5 (4 H, m, aryl H), 5.67 (1 H, s, olefinic H), 3.74 (6 H, s, 2 × OMe), 3.63 (3 H, s, OMe), 3.43 (2 H, s, CH_2), 2.65 (3 H, s, NMe), and 2.9—0.8 (8 H, m, aliphatic H). (ii) The yellow band (R_F 0.6) gave yellow needles (0.8 g) (from chloroform–ethanol) of *trimethyl 9-methyl-2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocyclopentane-4,10,11-tricarboxylate* (15), m.p. 169—170 °C (Found: C, 66.3; H, 5.6; N, 3.0. $C_{25}H_{25}NO_7$ requires C, 66.5; H, 5.6; N, 3.1%); $\nu_{max.}$ 1 715 cm^{-1} (s, broad); $\lambda_{max.}$ 246 (ε 22 600), 296 (6 200), 315 (4 400), and 455 nm (7 700); *m/z* 451 (M^+, 8%), 355 (100), 324 (24), and 237 (50) (Found: M − 96, 355.1089. $C_{19}H_{17}NO_6$ requires M, 355.1056); δ 8.59 (1 H, d, *J* 7.9 Hz), 7.38 (1 H, t, *J* 7.9 Hz), 6.78 (1 H, t, *J* 7.9 Hz), 6.60 (1 H, d, *J* 7.9 Hz), 5.39 (1 H, s), 3.87 (3 H, s, OMe), 3.84 (3 H, s, OMe), 3.81 (3 H, s, OMe), 3.19 (3 H, s, NMe), and 2.4—0.6 (8 H, m). Thermolysis of (15) (200 mg) gave an orange residue and a colourless distillate. The residue yielded pale yellow prisms (130 mg) (from ethanol) of trimethyl 9-methylcarbazole-1,2,4-tricarboxylate (42), m.p. 184—185 °C, identical (i.r., ^1H n.m.r., and mixed m.p.) with the ' compound (30) ' described in ref. 11. The distillate was obtained as colourless plates (30 mg) of the *cyclopentylketen dimer* (47), purified by sublimation at 110 °C (0.1 mmHg), m.p. 76—77 °C (Found: C, 74.9; H, 8.3. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%), $\nu_{max.}$ 1 738 cm^{-1} (s), *m/z* 192 (M^+, 38%), 164 (8), 136 (20), and 96 (100); δ 2.15—1.4 (m). $NaBH_4$ reduction of (15) gave compound (42) (140 mg). Compound (15) (0.3 g) was refluxed in glacial acetic acid for 3 days, and t.l.c. (chloroform) the carried out to give pale yellow prisms (0.23 g) of *trimethyl 2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocyclopentane-4,10,11-tricarboxylate* (19), m.p. 214—215 °C (Found: C, 66.0; H, 5.4; N, 3.4. $C_{24}H_{23}NO_7$ requires C, 65.9; H, 5.3; N, 3.2%); $\nu_{max.}$ 3 403 (s), 1 730 (s), and 1 710 cm^{-1} (s); $\lambda_{max.}$ 209 (ε 18 400), 244.5 (23 300), 295 (6 700), 314 (4 900), and 435 nm (8 900); *m/z* 437 (M^+, 10%), 341 (100), and 310 (85); δ 8.55 (1 H, dd, *J* 1.7, 7.0 Hz), 7.28 (1 H, dd, *J* 1.7, 7.4 Hz), 6.9—6.7 (2 H, m), 5.81 (1 H, s, exchanges with D_2O), 5.28 (1 H, s), 3.88 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.79 (3 H, s, OMe), and 2.1—1.0 (8 H, m). Methylation of (19) using dimethyl sulphate and phase-transfer catalysis (tetra-n-butylammonium hydrogen sulphate) [14] gave (15) in high yield. Thermolysis of (19) (100 mg) yielded a

Table 5. ^{13}C N.m.r. spectra of the new carbazoles, an indole, and the keten dimers, 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

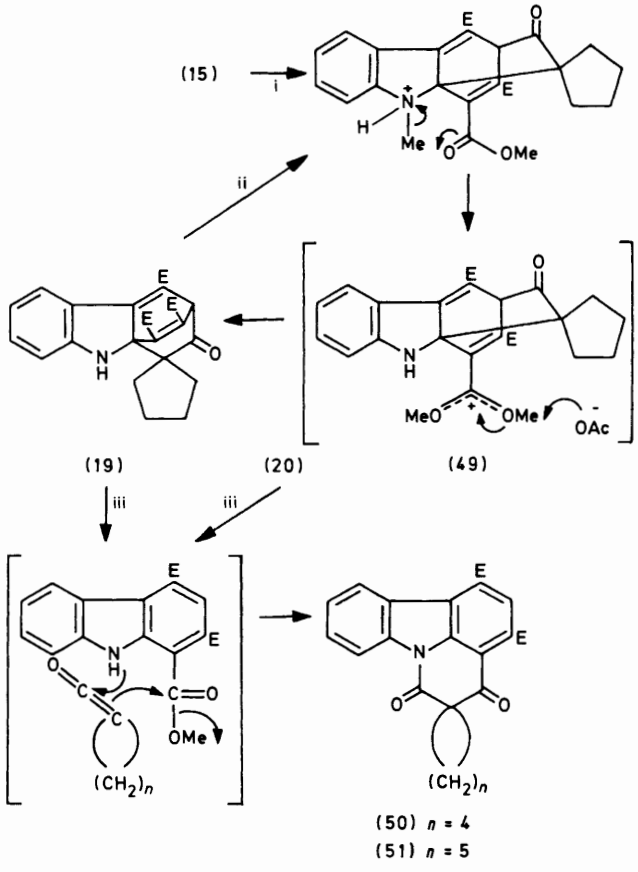
	Compounds								
Assignments	(6)	(41)	(42)	(43)	(44)	(47)	(48)	(50)	(51)
Ketone CO						216.5s	214.8s	192.6s	194.8s
Amide CO								171.1s	170.8s
Ester CO		168.6s	169.0s	169.1s	168.9s			167.6s	167.0s
		166.8s	167.3s	167.2s	166.8s			165.6s	165.8s
		165.8s	166.0s	166.2s	166.8s				
sp^2-C		142.2s	143.7s	140.4s	141.5s			140.3s	139.4s
	135.5s	137.4s	137.2s	136.4s	140.2s			139.3s	128.8s
	133.7s	125.7s	126.3s	126.5s	130.2s			139.3s	128.4s
	125.4s	125.7s	125.6s	125.6s	128.5s			129.3s	126.4s
	120.7s	125.2s	123.6s	123.1s	127.9s			128.7s	126.3s
	110.9s	124.3s	121.7s	(121.4s)$_2$	120.8s			123.6s	125.1s
		121.6s	120.1s	118.6s	113.6s			118.8s	123.8s
		113.2s							
sp^2-CH		131.4d	128.6d	126.1d	126.1d			130.1d	(130.2d)$_2$
	118.5d	128.8d	126.0d	123.8d	(121.4d)$_2$			126.2d	
	117.1d	123.6d	123.1d	122.8d	120.6d			126.2d	127.1d
	115.0d	110.2d	120.2d	120.2d	111.0d			125.0d	125.1d
			108.7d					115.9d	115.9d
OMe		53.0q	52.9q	52.9q	(52.8q)$_2$			53.0q	53.0q
		52.7q	52.6q	52.6q	52.5q			52.8q	52.8q
		52.6q	52.4q	52.3q					
NMe		30.6q	30.3q						
sp^3-C						79.7s	74.4s	66.4s	60.1s
sp^3-CH_2	41.0t			42.9t		33.2t	29.0t	(35.4t)$_2$	(30.9t)$_2$
	30.5t			24.8t		26.9t	25.2t		25.1t
	28.8t			22.7t			22.1t	(26.9t)$_2$	(22.0t)$_2$
	26.0t								
	25.8t								
	24.8t								
	(23.0t)$_2$								
	22.7t								

residue which sublimed at 240 °C to give pale yellow needles (70 mg) (from chloroform–ethanol) of *dimethyl* 4,6-*dioxo*-5,6-*dihydro*-4H-*pyrido*[3,2,1-jk]*carbazole*-5-*spirocyclopentane*-1,3-*dicarboxylate* (50), m.p. 162—163 °C (Found: C, 68.2; H, 4.75; N, 3.4. $C_{23}H_{19}NO_6$ requires C, 68.1; H, 4.7; N, 3.45%); $\nu_{max.}$ 1 740 (s), 1 721 (s), 1 718 (s), and 1 685 cm^{-1} (s); $\lambda_{max.}$ 219 shoulder (ε 29 600), 234.5 (32 400), 274 (18 600), and 399 nm (11 600); *m/z* 405 (M^+, 90%), 374 (20), 332 (100), and 309 (50); δ 8.75 (1 H, dd, *J* 2, 8 Hz), 8.55 (1 H, dd, *J* 2, 8 Hz), 8.09 (1 H, s), 7.7—7.2 (2 H, m), 4.08 (3 H, s, OMe), 3.98 (3 H, s, OMe), and 2.5—1.5 (8 H, m, 4 × CH_2). $NaBH_4$ reduction of (19) gave the carbazole (44) (100 mg), identical (^1H n.m.r., m.p., and i.r.) with the ' compound (29) ' described in ref. 11. Methylation of (44) (100 mg) using dimethyl sulphate and phase-transfer catalysis [14] (see above) gave compound (42) (65 mg).

(*b*) The indole (3) [5] (1 g) and DMAD (2 g) in refluxing 98% aqueous acetonitrile (80 ml) for 6 days followed by t.l.c. (chloroform) gave three crystalline products. (i) The yellow band (R_F 0.3) gave yellow rods (0.5 g) (from ethanol) of (Z,Z)-*dimethyl* 6,7-*bis*(*methoxycarbonyl*)-5-*methyl*-5,9,10,11,12,12a-*hexahydrocyclonona*[b]*indol*-12a-*ylmaleate* (27), m.p. 155—156 °C (Found: C, 64.85; H, 6.0; N, 2.85. $C_{26}H_{29}NO_8$ requires C, 64.6; H, 6.05; N, 2.9%); $\nu_{max.}$ 1 750 (m), 1 720 (s), 1 710 (s), and 1 675 cm^{-1} (s); $\lambda_{max.}$ 213 (ε 22 200) and 364 nm (13 300); *m/z* 483 (M^+, 85%), 452 (25), 425 (100), 393 (30), 365 (35), and 314 (72); δ 7.6—6.8 (4 H, m), 6.18 (1 H, s, olefinic H), 6.20 (1 H, dd, *J* 5, 12 Hz, olefinic H), 3.71 (9 H, s, 3 × OMe), 3.62 (3 H, s, OMe), 322 (3 H, s, NMe), and 3.2—1.0 (8 H, m). (ii) The orange band (R_F 0.4) gave orange rods (0.14 g) (from ethanol) of *tetramethyl* 5-*methyl*-5,7,8,9,10,10a-*hexahydrocyclohepta*[b]*indol*-6,10a-*diyldimaleate* (31), m.p. 145—146 °C (Found: C, 64.8; H, 6.3; N, 2.9. $C_{26}H_{29}NO_8$ requires C, 64.6; H, 6.05; N, 2.9%); $\nu_{max.}$ 1 732 (s) and 1 710 cm^{-1} (s); $\lambda_{max.}$ 208 (ε 15 900), 276.5 (8 300), and 415 nm (7 300); *m/z* 483 (M^+, 50%), 452 (20), 424 (100), 393 (20), 365 (25), 331 (30), and 271 (20); δ 7.3—6.5 (4 H, m), 6.14 (1 H, s, olefinic H), 5.41 (1 H, s, olefinic H), 3.84 (3 H, s, OMe), 3.72 (9 H, s, 3 × OMe), 3.01 (3 H, s, NMe), and 2.8—1.1 (8 H, m). (iii) The red band (R_F 0.8) gave red prisms (0.3 g) (from ethanol) of *dimethyl* 5-*methyl*-5,5a,6,7,8,9,10,10a-*octahydro*-5a,10a-*ethenocyclohepta*[b]*indole*-11,12-*dicarboxylate* (35), m.p. 97—98 °C (Found: C, 70.2; H, 6.8; N, 3.9. $C_{20}H_{23}NO_4$ requires C, 70.35; H, 6.8; N, 4.1%); $\nu_{max.}$ 1 695 cm^{-1} (s); $\lambda_{max.}$ 211 (ε 22 300), 240.5 (19 000), 307 (3 200), and 440 nm (1 600); *m/z* 341 (M^+, 100%) and 199 (33); δ 7.22—6.35 (4 H, m, aryl H), 3.75 (6 H, s, 2 × OMe), 2.92 (3 H, s, NMe), and 2.5—1.0 (10 H, m. aliphatic H).



Scheme 3. *Reagents:* i, heat



Scheme 4. *Reagents:* i, AcOH; ii, Me_2SO_4; iii, heat

Reaction of the Indole (4) *and Dimethyl Acetylenedicarboxylate.*—(*a*) The indole (4) (0.8 g) and DMAD (1.5 g) were refluxed in 98% aqueous methanol for 5 days [when all (4) had been consumed] and the mixture then evaporated and t.l.c. (chloroform–ethyl acetate, 19 : 1 v/v) carried out. Crystalline material was obtained from three bands. (i) The pale yellow band (R_F 0.2) gave colourless rods (0.25 g) (from ethanol) of *dimethyl* 3-*methoxycarbonylmethyl*-2-*oxo*-2,4,5,6,-7,7a,12,13-*octahydro*-11H-*furo*[2″,3″:2′,3′]*cyclohepta*-[1′,2′:4,5]*pyrrolo*[3,2,1-ij]*quinolin*-7a-*ylmaleate* (11), m.p. 138—139 °C (Found: C, 65.2; H, 6.0; N, 3.1. $C_{27}H_{29}NO_8$ requires C, 65.45; H, 5.9; N, 2.8%); $\nu_{max.}$ 1 770 (s) and 1 740 cm^{-1} (s); $\lambda_{max.}$ 212 (ε 28 000), 249 (9 100), and 310 nm (2 700); *m/z* 495 (M^+, 95%), 436 (100), and 377 (95); δ 7.08—6.58 (3 H, m), 5.76 (1 H, s, olefinic H), 3.72 (6 H, s), 3.64 (3 H, s), 3.40 (2 H, s), and 3.36—1.0 (14 H, m). The signal at δ 3.40 did not show any change in multiplicity on the addition of $Eu(fod)_3$. Compound (11) (0.1 g) was dissolved in chloroform (5 ml), in the presence of alumina (0.1 g) and left for 18 h. Evaporation yielded colourless needles (0.09 g) (from ethanol) of *dimethyl* 3-*methoxycarbonylmethyl*-2-*oxo*-2,4,5,6,7,7a,12,13-*octahydro*-11H-*furo*[2″,3″:2′,3′]*cyclohepta*[1′,2′:4,5]*pyrrolo*[3,2,1-ij]-*quinolin*-7a-*ylfumarate* (12), m.p. 162.5—163.5 °C (Found: C, 65.75; H, 6.2; N, 2.7. $C_{27}H_{29}NO_8$ requires C, 65.45; H, 5.9; N, 2.8%); $\nu_{max.}$ 1 765 (s), 1 735 (s), and 1 720 cm^{-1} (s); $\lambda_{max.}$ 212.5 (ε 26 200), 252 (8 700), and 313 nm (3 100); *m/z* 495 (M^+, 90%), 464 (20), 436 (100), and 377 (75); δ 7.0—6.45 (3 H, m), 6.59 (1 H, s, olefinic H), 3.74 (3 H, s), 3.69 (3 H, s), 3.45 (2 H, s), 3.19 (3 H, s), and 3.2—1.0 (14 H, m). (ii) The orange coloured band (R_F 0.6) yielded orange prisms (0.15 g) (from ethanol) of *trimethyl* 9-*oxo*-5,6,7a,8,9,10-*hexahydro*-7a,10-*etheno*-4H-*pyrido*[3,2,1-jk]*carbazole*-8-*spirocyclopentane*-11,12,13-*tricarboxylate* (16), m.p. 200—201 °C (Found: C, 67.6; H, 5.9; N, 2.8. $C_{27}H_{27}NO_7$ requires C, 67.9; H, 5.7; N, 2.9%); $\nu_{max.}$ 1 740 (s), 1 730 (s), and 1 705 cm^{-1} (s); $\lambda_{max.}$ 250 (ε 22 400), 310 (7 100), 322 (6 900), and 468 nm (10 000); *m/z* 477 (M^+, 2%), 381 (100), and 350 (10) (Found: M − 96), 381.1202. $C_{21}H_{19}NO_6$ requires M, 381.1212); δ 8.32 (1 H, d, J 8 Hz), 7.25 (1 H, d, J 8 Hz), 6.66 (1 H, t, J 8 Hz), 5.38 (1 H, s), 4.02—3.2 (4 H, m), 3.83 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.80 (3 H, s, OMe), and 2.9—0.8 (10 H, m). Thermolysis of compound (16) (120 mg) yielded a distillate of the dimer (47) (20 mg), and yellow prisms (80 mg) (from ethanol) of *trimethyl* 5,6-*dihydro*-4H-*pyrido*[3,2,1-jk]*carbazole*-8,9,11-*tricarboxylate* (43), m.p. 198.5—199.5 °C (Found: C, 66.1; H, 5.0; N, 3.7. $C_{21}H_{19}NO_6$ requires C, 66.1; H, 5.0; N, 3.7%); $\nu_{max.}$ 1 720 cm^{-1} (s); $\lambda_{max.}$ 218 (ε 18 900), 233 (24 600), 281.5 (21 900), 333 (14 000), and 390 nm (3 650); *m/z* 381 (M^+, 100%), 350 (20), and 263 (66); δ 8.62 (1 H, dd, J 2.2, 6.5 Hz, 5-H), 8.46 (1 H, s, 3-H), 7.35—7.1 (2 H, m), 4.25 (2 H, t, J 5.8, CH_2N), 4.08 (6 H, s, 2 × OMe), 3.97 (3 H, s, OMe), 3.10 (2 H, t, J 5.8 Hz), and 2.25 (2 H, pentet, J 5.8 Hz). $NaBH_4$ reduction of (16) gave the pyridocarbazole (43) (130 mg). (iii) The red band (R_F 0.75) yielded deep-red plates (0.05 g) (from ethanol) of *dimethyl* 5,6,7a,9,10,11,12,12a-*octahydro*-4H,8H-7a,12a-*ethenocyclohepta*[4,5]*pyrrolo*[3,2-ij]*quinoline*-13,14-*dicarboxylate* (36), m.p. 108—108.5 °C (Found: C, 72.1; H, 6.9; N, 3.8. $C_{22}H_{25}NO_4$ requires C, 71.9; H, 6.85; N, 3.8%); $\nu_{max.}$ 1 721 cm^{-1} (s); $\lambda_{max.}$ 212 (ε 22 000), 243 (2 600), 313 (12 000), and 460 nm (1 400); *m/z* 367 (M^+, 80%) and 225 (100); δ 6.97—6.52 (3 H, m), 3.77 (6 H, s), 3.4 (2 H, t, J 5.5 Hz), and 2.8—0.62 (14 H, m).

(*b*) When the indole (4) (0.8 g) was treated with DMAD (1.5 g) in 98% aqueous acetic acid (45 ml) at 100 °C for 4 days;

compounds (11) (1.5 g), (16) (0.5 g), and (36) (0.02 g) were isolated by t.l.c. as above.

(*c*) When indole (4) (1.0 g) was treated with DMAD (1.8 g) in refluxing 98% aqueous acetonitrile for 7 days followed by t.l.c., crystalline products were obtained from two bands. (i) The yellow band (R_F 0.3) yielded yellow prisms (0.25 g) (from ethanol) of (ZZ)-*methyl* 8,9-*bis*(*methoxycarbonyl*)-5,6,12,13,14,14a-*hexahydro*-4H,11H-*cyclonona*[4,5]*pyrrolo*-[3,2,1-ij]*quinolin*-14a-*ylmaleate* (28), m.p. 168.5—169.5 °C (Found: C, 66.2; H, 6.3; N, 2.55. $C_{28}H_{31}NO_8$ requires C, 66.0; H, 6.1; N, 2.75%); $\nu_{max.}$ 1 726 (s), 1 714 (s), and 1 686 cm^{-1} (s); $\lambda_{max.}$ 207 (ε 19 500) and 368 nm (14 000); *m/z* 509 (M^+, 100%), 450 (86), and 339 (60); δ 7.5—6.8 (3 H, m), 6.26 (1 H, s, olefinic H), 6.26 (1 H, dd, *J* 5, 12 Hz, olefin H), 3.72 (9 H, s), 3.62 (3 H, s), and 4.2—1.0 (14 H, m). (ii) The red band (R_F 0.75) gave the quinoline (36) (0.3 g).

Reaction of the Indole (5) *and Dimethyl Acetylenedicarboxylate*.—(*a*) The indole (5) (1.0 g) and DMAD (2.0 g) were refluxed in 95% aqueous acetonitrile (50 ml) for 7 days and the mixture then evaporated and t.l.c. (chloroform) carried out. From three of the bands crystalline material was obtained. (i) The yellow band (R_F 0.15) gave yellow prisms (0.40 g) (from ethanol) of (Z,Z)-*dimethyl* 6,7-*bis*(*methoxycarbonyl*)-5-*methyl*-9,10,11,12,13,13a-*hexahydro*-5H-*cyclodeca*[b]*indol*-13a-*ylmaleate* (29), m.p. 150—151 °C (Found: C, 64.95; H, 6.3; N, 2.7. $C_{27}H_{31}NO_8$ requires C, 65.15; H, 6.3; N, 2.8%); $\nu_{max.}$ 1 735 (s), 1 725 (s), 1 675 (s), and 1 630 cm^{-1} (s); $\lambda_{max.}$ 213 (ε 22 000) and 355 nm (12 800); *m/z* 497 (M^+, 100%), 466 (20), 438 (70), and 317 (75); δ 7.40—6.80 (4 H, m), 6.5 (1 H, dd, *J* 4, 11 Hz), 5.96 (1 H, s), 3.75 (3 H, s), 3.73 (3 H, s), 3.63 (6 H, s), 3.27 (3 H, s), and 2.6—0.6 (10 H, m). (ii) The yellow band (R_F 0.25) gave golden coloured prisms (0.30 g) (from ethanol) of *tetramethyl* 5-*methyl*-7,8,9,10,11,11a-*hexahydro*-5H-*cyclo*-*octa*[b]*indole*-6,11a-*diyldimaleate* (32), m.p. 158—159 °C (Found: C, 65.2; H, 6.5; N, 2.85. $C_{27}H_{31}NO_8$ requires C, 65.15; H, 6.3; N, 2.8%); $\nu_{max.}$ 1 730 (s) and 1 710 cm^{-1} (s); $\lambda_{max.}$ 211 (ε 16 000), 231 (13 000), 271 (10 000), and 408 nm (9 000); *m/z* 497 (M^+, 100%), 466 (20), 438 (98), and 406 (24); δ 7.28—6.48 (4 H, m), 6.16 (1 H, s, olefinic H), 5.44 (1 H, s, olefinic H), 3.84 (3 H, s), 3.73 (6 H, s), 3.64 (3 H, s), 3.06 (3 H, s), and 2.60—0.8 (10 H, m). (iii) The orange band (R_F 0.7) gave orange prisms (0.27 g) (from ethanol) of *dimethyl* 5-*methyl*-5a,6,7,8,9,10,11,11a-*octahydro*-5a,11a-*etheno*-5H-*cyclo*-*octa*[b]*indole*-12,13-*dicarboxylate* (37), m.p. 92—93 °C (Found: C, 70.8; H, 7.2; N, 4.15. $C_{21}H_{25}NO_4$ requires C, 70.95; H, 7.1; N, 3.95%); $\nu_{max.}$ 1 702 (s) and 1 625 cm^{-1} (s); $\lambda_{max.}$ 210 (ε 21 800), 240.5 (16 700), 307 (2 600), and 435 nm (1 200); *m/z* 355 (M^+, 69%) and 213 (100); δ 7.28—6.40 (4 H, m), 3.72 (6 H, s), 2.94 (3 H, s), and 2.8—0.6 (12 H, m).

(*b*) When the indole (5) (1 g) and DMAD (2 g) were refluxed in 98% aqueous methanol (50 ml) for 4 days, compounds (29) (0.2 g) and (32) (0.2 g) were isolated as described above.

(*c*) When the indole (5) (1 g) and DMAD (2 g) were left in 98% aqueous methanol for 14 days, isolation as described above yielded crystalline material from three bands. (i) The yellow band (R_F 0.15) gave compound (29) (0.28 g) and a colourless solid (20 mg), insoluble in ethanol, which was not further investigated. (ii) The darker yellow band (R_F 0.2) gave product (32) (50 mg). (iii) The orange band (R_F 0.5) gave yellow prisms (0.25 g) (from ethanol) of *dimethyl* 6-[1,2-*cis*-*bis*(*methoxycarbonyl*)*ethenyl*-5-*methyl*-7,8,9,10,11,11a-*hexahydro*-5H-*cyclo*-*octa*[b]*indol*-11a-*ylfumarate* (33), m.p. 129—130 °C (Found: C, 65.25; H, 6.35; N, 2.65. $C_{27}H_{31}NO_8$ requires C, 65.15; H, 6.3; N, 2.8%), $\nu_{max.}$ 1 731 (s) and 1 714 cm^{-1} (s); $\lambda_{max.}$ 211 (ε 17 600), 271 (11 800), and 314 nm (11 200); *m/z* 497 (M^+, 100%), 466 (14), 438 (72), and 407 (19); δ 7.50 (1 H, d, *J* 7.5 Hz), 7.19 (1 H, t, *J* 7.5 Hz), 6.70 (1 H, d, *J* 7.5 Hz), 6.68 (1 H, t, *J* 7.5 Hz), 6.58 (1 H, s, olefinic H), 5.42 (1 H, s, olefinic H), 3.83 (3 H, s, OMe), 3.72 (9 H, s, 3 × OMe), 3.07 (3 H, s, NMe), and 3.0—0.8 (10 H, m, aliphatic H).

(*d*) The indole (5) (1 g) and DMAD (2 g) were left at room temperature in 98% aqueous acetic acid for 30 days and then neutralised with $NaHCO_3$ and extracted with chloroform. Evaporation and t.l.c. (chloroform) gave crystalline products from four bands. (i) The band (R_F 0.15) gave the cyclodeca-compound (29) (30 mg). (ii) The band (R_F 0.25) gave the cyclo-octa-compound (32) (50 mg). (iii) The orange band (R_F 0.5) gave orange prisms (20 mg) (from ethanol) of *trimethyl* 9-*methyl*-2-*oxo*-1,2,3,9a-*tetrahydro*-3,9a-*ethenocarbazole*-1-*spirocyclohexane*-4,10,11-*tricarboxylate* (17), m.p. 190—191 °C (decomp.) (Found: C, 67.1; H, 5.9; N, 2.9. $C_{26}H_{27}NO_7$ requires C, 67.1; H, 5.9; N, 3.0%); $\nu_{max.}$ 1 740 (s), 1 722 (s), and 1 710 cm^{-1} (s); $\lambda_{max.}$ 210 (ε 15 000), 245 (23 000), 296 (5 800), 318 (4 300), and 455 nm (6 500); *m/z* 465 (M^+, 0.5%), 355 (100), and 324 (10); δ 8.62 (1 H, d, *J* 8.0 Hz), 7.4 (1 H, t, *J* 8.0 Hz), 6.80 (1 H, t, *J* 8.0 Hz), 6.61 (1 H, d, *J* 8.0 Hz), 5.30 (1 H, s), 3.79 (3 H, s, OMe), 3.72 (3 H, s, OMe), 3.76 (3 H, s, OMe), 3.28 (3 H, s, NMe), and 2.2—0.9 (10 H, m, aliphatic H). Thermolysis of the spiro-compound (17) (0.30 g) gave a residue of yellow prisms (180 mg), m.p. 184—185 °C, of the carbazole (42) and a volatile product as colourless plates (50 mg), the *cyclohexylketen dimer* (48), m.p. 154—155 °C (Found: C, 76.0; H, 8.95. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); $\nu_{max.}$ 1 738 cm^{-1} (s); *m/z* 220 (18%), 192 (14), 164 (14), and 110 (100); δ 2.2—1.0 (m). $NaBH_4$ reduction of compound (17) gave the carbazole (42) (120 mg). On refluxing (17) (0.30 g) in glacial acetic acid for 3 days, followed by evaporation and t.l.c., (42) (0.20 g) was obtained. (iv) The yellow band (R_F 0.8) gave pale yellow needles (0.55 g) (from ethanol) of *dimethyl* 5-*methyl*-7,8,9,10,11,11a-*hexahydro*-5H-*cyclo*-*octa*[b]*indol*-11a-*ylmaleate* (40), m.p. 117—118 °C (Found: C, 71.2; H, 7.2; N, 3.8. $C_{21}H_{25}NO_4$ requires C, 70.95; H, 7.1; N, 3.95%); $\nu_{max.}$ 1 728 (s), 1 674 (m), and 1 634 cm^{-1} (m); $\lambda_{max.}$ 211 (ε 17 000) and 281 nm (23 700); on the addition of one drop of perchloric acid the u.v. spectrum changed to $\lambda_{max.}$ 214 (15 620) and 288.5 nm (6 000); *m/z* 355 (M^+, 100%) and 296 (62); δ 7.4—6.3 (4 H, m, aryl H), 6.1 (1 H, s, olefinic H), 4.46 (1 H, t, *J* 8 Hz, olefin H), 3.71 (3 H, s, OMe), 3.65 (3 H, s, OMe), 2.97 (3 H, s, NMe), and 2.6—0.6 (10 H, m, aliphatic H). Treatment of the cyclo-octaindole (40) (100 mg) with DMAD (0.5 g) in 98% aqueous acetic acid (10 ml) for 14 h at 80 °C gave compounds (32) (50 mg) and (29) (40 mg).

(*e*) Treatment of the indole (5) (0.8 g) with DMAD (1.5 g) in 98% aqueous acetic acid for 5 days at 80 °C followed by evaporation under reduced pressure and t.l.c. gave compounds (17) (0.45 g), (32) (50 mg), (40) (120 mg), and (29) (45 mg).

(*f*) The indole (5) (1 g) was refluxed in 98% aqueous acetic acid with DMAD (2 g) for 3 days and the mixture then evaporated and t.l.c. carried out to give compounds (17) (0.3 g) and (42) (0.3 g) as the only isolable products.

Reaction of the Indole (6) *and Dimethyl Acetylenedicarboxylate*.—(*a*) The indole (6) (0.8 g) and DMAD (1.5 g) in 98% aqueous acetic acid were kept at 100 °C for 4 days and the mixture then evaporated and t.l.c. (chloroform–ethyl acetate, 19 : 1 v/v) carried out. Crystalline products were obtained from four bands. (i) The yellow band (R_F 0.15) gave pale yellow prisms (0.24 g) (from ethanol) of (Z,Z)-*dimethyl* 8,9-*bis*(*methoxycarbonyl*)-5,6,11,12,13,14,15,15a-*octahydro*-4H-*cyclodeca*-[4,5]*pyrrolo*[3,2,1-ij]*quinolin*-15a-*ylmaleate* (30), m.p. 207—208 °C (Found: C, 66.4; H, 6.3; N, 2.9. $C_{29}H_{33}NO_8$ requires C, 66.5; H, 6.35; N, 2.7%); $\nu_{max.}$ 1 732 (s) and 1 712 cm^{-1} (s);

$\lambda_{max.}$ 209 (ε 18 000) and 366 nm (15 500); *m/z* 523 (M^+, 70%), 464 (60), and 353 (100); δ 7.3—6.9 (3 H, m), 6.46 (1 H, dd, *J* 6, 14 Hz, olefinic H), 6.0 (1 H, s, olefinic H), 3.77 (3 H, s), 3.72 (3 H, s), 3.64 (6 H, s), and 3.4—0.6 (16 H, m). (ii) The yellow band (R_F 0.25) gave golden yellow prisms (0.17 g) (from ethanol) of *tetramethyl* 5,6,9,10,11,12,13,13a-*octahydro*-4H-*cyclo-octa*[4,5]*pyrrolo*[3,2,1-ij]*quinolin*-8,13a-*diyldimaleate*. (34), m.p. 163—164 °C (Found: C, 66.2; H, 6.5; N, 2.6, $C_{29}H_{33}NO_8$ requires C, 66.5; H, 6.35; N, 2.7%); $\nu_{max.}$ 1 731 (s) and 1 711 cm^{-1} (s); $\lambda_{max.}$ 209 (ε 16 000), 243 (9 700), 279 (8 600), and 418 nm (6 600); *m/z* 523 (M^+, 100%), 492 (12), and 464 (90); δ 7.0—6.6 (3 H, m), 6.12 (1 H, s, olefinic H), 5.30 (1 H, s, olefinic H), 3.82 (3 H, s), 3.72 (6 H, s), 3.61 (3 H, s), 3.38—3.08) (2 H, m), and 2.8—1.0 (14 H, m). (iii) The orange band (R_F 0.5) yielded orange prisms (0.15 g) (from ethanol) of *trimethyl* 9-*oxo*-5,6,7a,8,9,10-*hexahydro*-7a,10-*etheno*-4H-*pyrido*[3,2,1-ij]*carbazole*-8-*spirocyclohexane*-11,12,-13-*tricarboxylate* (18), m.p. 183—184 °C (Found: C, 68.1; H, 5.9; N, 2.8. $C_{28}H_{29}NO_7$ requires C, 68.4; H, 5.95; N, 2.85%); $\nu_{max.}$ 1 730 (s), 1 710 (s), and 1 705 cm^{-1} (s); $\lambda_{max.}$ 240 (ε 22 000), 305 (6 400), 325 (5 400), and 470 nm (9 700); *m/z* 491 (M^+, 2%), 381 (100), and 350 (10); δ 8.30 (1 H, d, *J* 7 Hz), 7.05 (1 H, d, *J* 7 Hz), 6.64 (1 H, t, *J* Hz), 5.25 (1 H, s), 3.78 (3 H, s, OMe), 3.80 (3 H, s, OMe), 3.82 (3 H, s, OMe), and 2.85—0.8 (16 H, m). Thermolysis of the quinoline (18) (90 mg) yielded a yellow residue, m.p. 198—200 °C of the pyridocarbazole (43) (50 mg) and a volatile product, m.p. 154—155 °C, the dimer (48) (20 mg). $NaBH_4$ reduction of (18) gave (43) (90 mg). (iv) The red band (R_F 0.7) gave deep-red prisms (0.12 g) (from ethanol) of *dimethyl* 5,6,7a,8,9,10,11,12,13,13a-*decahydro*-4H-7a,13a-*ethenocyclo-octa*[4,5]*pyrrolo*[3,2,1-ij]-*quinoline*-14,15-*dicarboxylate* (38), m.p. 129—130 °C (Found: C, 72.1; H, 7.35; N, 4.0. $C_{23}H_{27}NO_4$ requires C, 72.4; H, 7.15; N, 3.7%); $\nu_{max.}$ 1 728 (s), 1 711 (s), and 1 700 cm^{-1} (s); $\lambda_{max.}$ 212 (ε 24 000), 244 (14 500), 310 (3 020), and 465 nm (2 550); *m/z* 381 (M^+, 71%) and 239 (100); δ 7.00—6.56 (3 H, m), 3.75 (6 H, s), 3.38 (2 H, t, *J* 6.5 Hz), 2.7 (2 H, t, *J* 6.5 Hz), and 2.5—1.0 (14 H, m).

(*b*) When the indole (6) (1.0 g) was treated with DMAD (2.2 g) in refluxing 98% aqueous methanol (40 ml) and the products isolated as above, the same products were obtained as follows: (38) (0.08 g), (18) (0.2 g), (30) (0.24 g), and (34) (0.34 g).

(*c*) When the indole (6) (1 g) was refluxed with DMAD (2 g) for 3 days in 98% aqueous acetonitrile (50 ml), the products isolated were (38) (0.43 g), (30) (0.52 g), and (34) (0.45 g).

Trimethyl 6-*Bromo*-9-*methylcarbazole*-1,2,4-*tricarboxylate*. —Thermolysis of trimethyl 6-bromo-9-methyl-2-oxo-1,2,3,9a-tetrahydro-3,9a-ethenocarbazole-1-spirocycloheptane-4,10,11-tricarboxylate [8] (14) (250 mg) gave a residue of yellow prisms (150 mg) (from chloroform–ethanol) of *trimethyl* 6-*bromo*-9-*methylcarbazole*-1,2,4-*tricarboxylate* (41), m.p. 223—224 °C (Found: C, 52.9; H, 3.8; Br, 18.8; N, 3.25. $C_{19}H_{16}BrNO_6$ requires C, 52.6; H, 3.7; Br, 18.4; N, 3.25%); $\nu_{max.}$ 1 731 (s) and 1 721 cm^{-1} (s); $\lambda_{max.}$ 218 (ε 17 400), 231 (24 100), 277 (17 400), 328 (10 400), and 387 nm (2 900); *m/z* 433/435 (M^+, 100%), 402/404 (27), 374/376 (40), and 315/317 (40); δ 9.04 (1 H, d, *J* 0.8 Hz), 8.48 (1 H, s), 7.68 (1 H, dd, *J* 0.8, 7.0 Hz), 7.30 (1 H, d, *J* 7.9 Hz), 4.10 (6 H, s, 2 × OMe), 4.00 (3 H, s, OMe), and 3.84 (3 H, s, NMe). A volatile product (47) (25 mg) was also isolated. $NaBH_4$ reduction of (14) gave (41) (80 mg).

Reaction of the Indole (8) *and Dimethyl Acetylenedicarboxylate*.—The indole (8) (1 g) and DMAD (2 g) were allowed to react in 98% aqueous acetic acid (50 ml) at 80 °C for 1½ days (or at room temperature for 14 days) and the mixture then evaporated under reduced pressure and t.l.c. (chloroform) carried out to give (8) (0.3 g) and yellow prisms (R_F 0.5) (0.8 g) of *trimethyl* 2-*oxo*-1,2,3,9a-*tetrahydro*-3,9a-*ethenocarbazole*-1-*spirocyclohexane*-4,10,11-*tricarboxylate* (20), m.p. 216—217 °C (Found: C, 66.8; H, 5.55; N, 2.8. $C_{25}H_{25}NO_7$ requires C, 66.5; H, 5.6; N, 3.1%); $\nu_{max.}$ 3 195 (m), 1 700 (s), and 1 710 cm^{-1} (s); $\lambda_{max.}$ 208 (ε 18 400), 244 (24 100), 296 (6 350), 315 (3 800), and 433 nm (6 660); *m/z* 451 (M^+, 5%), 341 (100), 310 (85), 251 (40), and 223 (55); δ 8.54 (1 H, dd, *J* 7, 1, 5-H), 7.34—6.85 (3 H, m, aryl H), 5.83 (1 H, broad, NH), 5.19 (1 H, s, 3-H), 3.88 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.78 (3 H, s, OMe), and 2.0—0.6 (10 H, m, aliphatic H). Thermolysis of the spiro-compound (20) (450 mg) gave a volatile product (30 mg), m.p. 154—155 °C, identical with the dimer (48), and a yellow residue which separated on t.l.c. (chloroform) to give a yellow band (R_F 0.5), from which the carbazole (44) (210 mg) was obtained, together with a pale yellow band (R_F 0.6) from which colourless prisms (80 mg) were obtained (from ethanol) of *dimethyl* 4,6-*dioxo*-5,6-*dihydro*-4H-*pyrido*[3,2,1-jk]-*carbazole*-5-*spirocyclohexane*-1,3-*dicarboxylate* (51), m.p. 220—221 °C (Found: C, 68.7; H, 5.15; N, 2.95. $C_{24}H_{21}NO_6$ requires C, 68.7; H, 5.05; N, 3.35%); $\nu_{max.}$ 1 734 (s), 1 720 (s), and 1 691 cm^{-1} (s); $\lambda_{max.}$ 219 shoulder (ε 21 400), 236 (31 700), 275 (10 200), and 338 nm (8 800); *m/z* 419 (M^+, 100%), 388 (20), and 332 (80); δ 8.87 (1 H, dd, *J* 1, 7 Hz), 8.60 (1 H, dd, *J* 1, 7 Hz), 8.29 (1 H, s), 7.65 (1 H, dt, *J* 1, 7.7 Hz), 7.46 (1 H, dt, *J* 1, 7.7 Hz), 4.09 (3 H, s, OMe), 3.99 (3 H, s, OMe), and 2.3—1.0 (10 H, m). $NaBH_4$ reduction of (20) gave (44) (90 mg).

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