Addition Reactions of Heterocyclic Compounds. Part 78.[1] Reaction of Dimethyl Acetylenedicarboxylate with Some Cyclopent[b]indoles and Cyclohex[b]indoles and the Crystal Structure of (Z)-Methyl 1-Methoxycarbonylmethyl-11-methoxycarbonylmethylene-12-oxo-1,1a,1b,2,3,4,4a,8,9,9a-decahydro-1b,4a-epoxyethanoindolizino-[2,3,4,5,6-jklm]carbazole-1-carboxylate

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Reaction of 5,6,9,10-tetrahydro-4H,8H-cyclopenta[4,5]pyrrolo[3,2,1-ij]quinoline and 5,6,8,9,10,11-hexahydro-4H-pyrido[3,2,1-jk]carbazole with dimethyl acetylenedicarboxylate in aqueous methanol or acetic acid gave five new lactones and a phenanthridone diketone. In aqueous methanol and acetonitrile the carbazole gave three closely related (1 + 2 DMAD − CH₂) adducts of a type not previously encountered. The structure of one of these was established by X-ray crystallography; their formation, which includes C-alkylation of a CH₂N group, is discussed. The cyclopentene, and also its N-methyl analogue, yielded a new type of (1 + DMAD + H₂O) adduct possessing a 1-benzazocin-2-one system. A novel (1 + 3 DMAD) adduct was also isolated. All 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 n.m.r. spectra.

Having shown [2] that the addition of dimethyl acetylenedicarboxylate (DMAD) to the N-methylindoles (1) and (2) gives rise mainly to a variety of (1 + 1 DMAD − CH₂) lactones formed by initial electrophilic attack of DMAD at position-3, and that addition to the strained tetracyclic indole (3) gives rise to a very different array of products,[3] all formed by cleavage of the 1,2-bond of the indole ring at some stage during the reaction, we were interested to see how the homologous tetracyclic indoles (4) and (5) would react with DMAD.

The cyclopentene (4) and DMAD in either wet methanol or wet acetic acid gave two lactones, (6) (orange) and (7) (yellow), identified from their close spectral similarity with the adducts from (1),[2] and from their lactone carbonyl carbon atom ¹³C–¹H coupling constants [4] (Table 1). In wet acetonitrile, compound (4) gave (7), and a minor product A, which was formed by the addition of one mole of DMAD and one mole of water to the indole. From the spectral data, this product A is clearly different from previously isolated DMAD–indole adducts in which addition of water has also occurred, viz. (1 + 1 DMAD + H₂O) [3] and (1 + 2 DMAD + H₂O),[3] as it possesses no ketone or hydroxy-function. However, all the data, including the ¹H and ¹³C n.m.r. spectra (see Table 2), fit structure (11) or its geometrical isomer (12), which furthermore, may be regarded as being formed by a series of processes (see Scheme 1) which are consistent with the accepted mode of formation of our previously described structures,[2,3] several of which have been confirmed by X-ray crystallography.[5,6] This involves firstly 3-substitution of the indole ring and quenching of the iminium ion by hydroxyl, giving the cyclopentindole (15), from which compounds (6) and (7) may be formed by lactonisation, and (11) and (12) by an alternative process involving cleavage of the 2,3-bond of the indole ring as indicated, a process which has not previously been observed in the formation of DMAD–indole adducts. The geometrical isomerism present in structures (11) and (12) cannot, unfortunately, be resolved by spectroscopic methods.

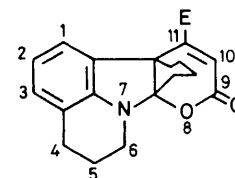This ring-opening reaction appears to be associated with the cyclopent[b]indoles in wet acetonitrile, since indole (1)
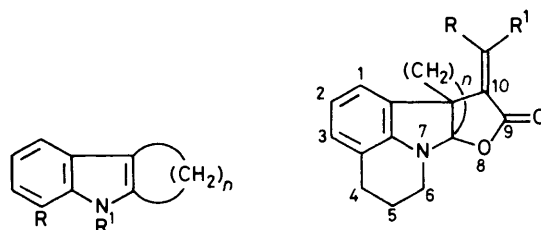
(1) R=H, R¹=Me, n =3
(2) R=H, R¹=Me, n =4
(3) R,R¹=(CH₂)₂, n=4
(4) R,R¹ = (CH₂)₃, n=3
(5) R,R¹ = (CH₂)₃, n=4

(6) R=E, R¹=H, n=3
(7) R=H, R¹=E, n=3
(8) R=H, R¹=CO₂H, n=4
(9) R=H, R¹=E, n=4
(10) R=E, R¹=H, n = 4
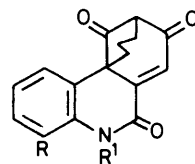
(17) R,R¹ = (CH₂)₃
(18) R,R = (CH₂)₂

(19)

E = CO₂Me

also yields a (1 + 1 DMAD + H₂O) adduct, B, with spectral data showing appropriate correspondence with that of (11) or (12), and which consequently has structure (13) or (14). Compound (16),[2] an analogue of (7), was also isolated, being the major product from the reaction.

The carbazole (5) in wet acetic acid gave as the main product the trione (17), identified from a comparison of its spectra (see Table 2 for ¹³C n.m.r. data) with those of the

Table 1. ^{13}C N.m.r. data of (1 + 1 DMAD − CH$_2$) lactones and their derivatives. Measured for solutions in CDCl$_3$ at 22.63 MHz and recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

Assignments	Compounds					
	(6)	(7)	(8)	(9)	(10)	(19)
Lactone CO	169.8 s [a]	167.1 s [c]	170.7 s [e]	165.5 s [g]	168.8 s [i]	163.2 s [k]
Acid CO			163.4 s [f]			
Ester CO	165.1 s [b]	165.6 s [d]		165.7 s [h]	165.5 s [j]	165.5 s [l]
sp^2-C	147.7 s	145.7 s				
	146.2 s	140.7 s	143.8 s	144.5 s	144.6 s	146.7 s
	128.0 s	127.4 s	143.0 s	139.4 s	144.1 s	144.8 s
	118.0 s	118.4 s	129.3 s	130.6 s	129.6 s	129.2 s
			121.4 s	120.8 s	119.9 s	120.5 s
sp^2-CH	128.2 d	128.0 d	129.1 d	127.9 d	128.0 d	127.5 d
	124.9 d	126.9 d	128.6 d	124.4 d	125.3 d	124.7 d
	123.2 d	120.5 d	120.8 d	120.5 d	122.6 d	121.7 d
	118.7 d	118.6 d	120.6 d	115.9 d	119.7 d	119.8 d
sp^3-C-N(-O)	115.1 s	114.6 s	113.8 s	107.2 s	107.8 s	107.0 s
sp^3-C	63.1 s	62.8 s	57.3 s	55.3 s	56.7 s	59.6 s
OCH$_3$	52.2 q	52.3 q		52.4 q	52.2 q	52.5 q
sp^3-CH$_2$	39.9 t	40.2 t	39.8 t	39.6 t	39.7 t	38.9 t
	39.1 t	40.0 t	32.1 t	32.1 t	29.7 t	33.1 t
	34.9 t	35.3 t	29.6 t	29.6 t	29.0 t	29.2 t
	25.9 t	25.7 t	24.2 t	24.3 t	24.3 t	24.4 t
	24.2 t	24.1 t	27.3 t	22.5 t	22.4 t	22.3 t
	22.2 t	22.1 t	21.5 t	21.4 t	20.2 t	22.2 t
			20.3 t	20.3 t	19.7 t	21.3 t

Coupling constants from proton-coupled spectra.

[a] d, $J_{CO,H}$ 7.0. [b] dq, $J_{CO,Me}$ 4.0; $J_{CO,H}$ 1.2. [c] d, $J_{CO,H}$ 12.5. [d] dq, $J_{CO,Me}$ 4.0; $J_{CO,H}$ 1.8. [e] d, $J_{CO,H}$ 13.2. [f] s. [g] d, $J_{CO,H}$ 12.3. [h] dq, $J_{CO,Me}$ 4.0; $J_{CO,H}$ 1.9. [i] d, $J_{CO,H}$ 7.8. [j] dq, $J_{CO,Me}$ 4.0; $J_{CO,H}$ 1.2. [k] d, $J_{CO,H}$ 3.1. [l] dq, $J_{CO,Me}$ 3.9; $J_{CO,H}$ 10.5.
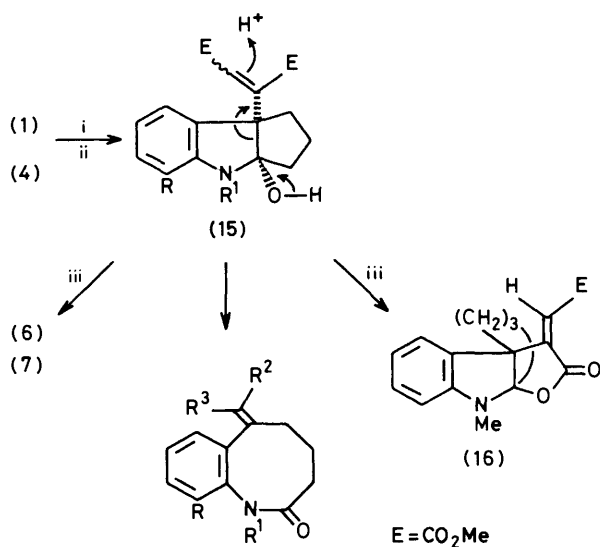
(11) R,R^1 = (CH$_2$)$_3$, R^2=CH$_2$E, R^3=E
(12) R,R^1 = (CH$_2$)$_3$, R^2=E, R^3=CH$_2$E
(13) R=H, R^1=Me, R^2=CH$_2$E, R^3=E
(14) R=H, R^1=Me, R^2=E, R^3=CH$_2$E

Scheme 1. *Reagents*: i, EC≡CE; ii, H$_2$O; iii, −MeOH

analogue (18), the structure of which has been established [3,6] by X-ray crystallography. A minor product was the acid (8) with spectra very similar to that of the acid previously obtained from the indole (2),[2] and further identified from its reaction with diazomethane which gave compound (9) (see

Table 1 for ^{13}C n.m.r.). In 90% aqueous methanol the carbazole (5) gave two (1 + 1 DMAD − CH$_2$) lactones (10) and (19), and two more polar adducts C and D (see later) which were the major products. The lactones were assigned the structures (10) and (19) on the basis of their ^{13}C n.m.r. spectra including ^{13}C-^{1}H coupling constants (see Table 1), and close spectral similarity to the analogous γ- and δ-lactones obtained from DMAD and the indole (2).[2] In aqueous methanol (2% water) only products C and D were obtained. From the reaction in wet acetonitrile (15% water), C, D, E, and (19) were isolated. In much drier acetonitrile (containing 2% water), the indole (5) gave (19), E, and F as the only isolable products. Compound E, formed by addition of two moles of DMAD to the carbazole and loss of 'CH$_2$', is however quite different from the (1 + 2 DMAD − CH$_2$) lactone (20) [2,5] isolated from indole (2), since its ^{13}C n.m.r. spectrum (Table 3) shows signals for two sp^3-CH groups (both doublets at δ 65.8 and 50.7 p.p.m.), and its lactone carbonyl is strongly coupled (12.5 Hz) to the olefinic proton. As no single structure for compound E could be deduced with confidence from spectroscopic methods, its structure was determined by X-ray crystallography. The resultant structure (21) and stereochemistry is shown in the Figure. The most unusual feature is a new C−C bond from the original N-methylene group to a DMAD fragment. The configuration at the nitrogen atom is distinctly pyramidal. The pyrrolo-ring B is nearly planar (maximum deviation from mean plane $\Delta_{max.}$ = 0.11 Å) and makes a dihedral angle of 8.5° with the adjacent aromatic ring A. In contrast, the other pyrrolo-ring D is in the form of an envelope. The lactone ring together with its exocyclic olefinic and carbonyl double bonds closely attains planarity ($\Delta_{max.}$ = 0.11 Å). In consequence of C/D *cis*-fusion, both six-membered rings C and E take somewhat distorted twist-boat conformations to alleviate intramolecular overcrowding. All bond distances and angles (Table 4) are in agreement with commonly accepted values, and there are no unusual intermolecular

Table 2. [13]C N.m.r. spectra for solutions in CDCl₃ measured at 22.63 Hz and recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

Assignment	(17)	A (11) or (12)	B (13) or (14)	F (38) or (39)
Ketone CO	203.0 s			
	197.5 s			
Amide NCO	158.6 s [a]	173.5 s [b]*	173.1 s [e]*	
Ester CO		170.7 s [c]	170.4 s [f]	167.9 s
		166.8 s [d]	166.4 s [g]	167.1 s
				166.4 s
				165.7 s
				165.5 s
				164.3 s
sp²-C	146.2 s	152.9 s	152.4 s	165.5 s
	132.6 s	137.7 s	140.0 s	150.3 s
	125.5 s	135.4 s	139.6 s	146.7 s
	121.3 s	135.0 s	123.8 s	140.4 s
		123.7 s		139.7 s
				134.5 s
				132.9 s
				122.3 s
				96.1 s
sp²-CH	134.1 d	127.0 d	128.8 d	127.4 d
	129.3 d	126.5 d	127.9 d	123.4 d
	128.1 d	125.6 d	127.8 d	122.6 d
	122.9 d		125.3 d	122.3 d
				121.2 d
sp³-C	54.6 s			60.3 s
sp³-CH	62.4 d			
OCH₃		51.8 q	51.5 q	52.5 q
		51.7 q	51.4 q	52.3 q
				51.9 q
				51.8 q
				51.8 q
				51.2 q
NCH₃			36.4 q	
sp³-CH₂	42.6 t	42.6 t	36.6 t	48.5 t
	40.7 t	36.2 t	35.6 t	34.9 t
	32.1 t	35.6 t	33.5 t	30.6 t
	27.6 t	35.0 t	24.2 t	24.3 t
	20.5 t	27.1 t		22.5 t
	16.6 t	24.4 t		19.6 t
		24.4 t		

Coupling constants from proton-coupled spectra.

[a] d, $J_{CO,H}$ 5.9. [b] m. [c] Sextet, J_{CO,CH_2} 4.1; $J_{CO,Me}$ 4.1. [d] q, $J_{CO,Me}$ 3.5. [e] m. [f] Sextet, $J_{CO,Me}$ 4.1. [g] q, $J_{CO,Me}$ 4.1.

* Irradiation at 2.1—3.0 p.p.m. caused the multiplet to collapse to a narrow ($W_\frac{1}{2}$ = 2 Hz) ill-defined singlet.

Table 3. [13]C N.m.r. data of (1 + 2 DMAD − CH₂) adducts. Measured for solutions in CDCl₃ at 22.63 MHz and recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

Assignments	E (21)	C (22, 23, or 24)	D (25, 26, or 27)
Lactone CO	161.1 s [a]	165.8 s [e]	168.7 s [i]
Ester CO	171.6 s [b]	175.1 s [f]	175.1 s [j]
	171.2 s [c]	171.4 s [g]	171.4 s [k]
	165.5 s [d]	165.4 s [h]	165.1 s [l]
sp²-C	147.0 s	147.7 s	148.1 s
	140.6 s	140.3 s	145.1 s
	129.2 s	128.4 s	128.0 s
	121.8 s	121.6 s	120.9 s
sp²-CH	128.2 d	127.9 d	126.8 d
	126.1 d	126.5 d	126.6 d
	120.3 d	120.4 d	124.2 d
	119.9 d	120.2 d	119.7 d
sp³-C–N(–O)	113.6 s	113.3 s	114.2 s
sp³-C	60.2 s	57.6 s	57.5 s
	54.8 s	53.6 s	54.2 s
sp³-CH	65.8 d	60.7 d	60.8 d
	50.7 d	49.1 d	49.0 d
OCH₃	52.3 q	52.9 q	53.0 q
	51.6 q	52.3 q	52.2 q
	51.3 q	52.0 q	52.0 q
sp³-CH₃	43.6 t	35.3 t	35.4 t
	32.0 t	29.5 t	26.8 t
	25.3 t	25.3 t	25.5 t
	25.0 t	23.8 t	23.9 t
	21.9 t	19.2 t	18.9 t
	18.4 t	17.9 t	17.9 t

Coupling constants from proton-coupled spectra.

[a] d, $J_{CO,H}$ 12.5. [b] m. [c] m. [d] dq, $J_{CO,H}$ 1.5; $J_{CO,Me}$ 3.9. [e] d, $J_{CO,H}$ 11.4. [f] m. [g] m. [h] dq, $J_{CO,H}$ 1.6; $J_{CO,Me}$ 4.0. [i] d, $J_{CO,H}$ 7.3. [j] m. [k] m. [l] dq, $J_{CO,H}$ 1.0; $J_{CO,Me}$ 3.9.

contacts. This structure (21) is completely consistent with all spectral data. Its formation may be rationalised (see Scheme 2), by, once again, initial attack of DMAD at the 3-position of the indole, leading to the enamine (28) and subsequent attack by a second mole of DMAD, giving the familiar [2] zwitterion (29), which, by a sterically favoured proton shift could yield the ylide (30). Direct cyclisation would be expected to give a 5-membered ring,[7] and addition of water, followed by lactonisation, leads to compound (21). Alternatively, the zwitterion (30) could tautomerise to (31), a 1,5-dipole stabilised by delocalisation as in structure (32), before undergoing a symmetry-allowed disrotatory electrocyclisation to the product (33) and eventual formation of (21) via hydration and lactonisation. This cyclisation to compound (33) has an exact analogy in the thiophen series.[8] However, one might expect (30) to protonate rather than tautomerise. An alternative route to compound (30) begins with an ene-type reaction

of DMAD and the carbazole (28) leading to an aziridine (34) which by a well known process, could ring-open to give the required product. Clearly the formation of (21) can be accounted for, but the exact order of the steps and which of the various routes is more likely to be correct does not warrant further speculation at this stage.

Compounds C and D are both (1 + 2 DMAD − CH₂) adducts, and exhibit remarkably similar mass, i.r., u.v. and ¹H and ¹³C n.m.r. spectra, to these of the indolizinocarbazole (21). This includes all ¹³C n.m.r. multiplicities (see Table 3) and indicates that C and D have structures very similar to that of (21). Like (21), compound C also exhibits a lactone CO which is strongly coupled (11.4 Hz) to the olefinic proton, showing a *trans*-arrangement of these groups. In fact, a comparison of the spectral data reveals that the only difference between compounds C and (21) is in the chemical shift of a few n.m.r. resonances: the ¹³C signals at δ 35.3 (t), 57.6 (s), 60.7 (d), and 175.1 (s) [compared with δ 43.6 (t), 60.2 (s), 65.8 (d), and 171.6 (s) for (21)] are the only signals differing by more than 2.5 p.p.m., and the ¹H n.m.r. signals at δ 4.90 (dd), 2.98 (1 H, d), and 2.52 (1 H, d) [compared with δ 3.97 (dd) and 3.15 (2 H, s) for (21)] are the only significantly different ones. The ¹³C n.m.r. signals from compound (21) listed above may be respectively assigned to the following structural features: CH_2E (confirmed by observing the enhancement of the ¹³C signal on selectively irradiating the methylene singlet at δ 3.15), C-1, C-9a (confirmed by selective irradiation at δ 3.97), and one of the ester carbonyls attached to C-1. This suggests that the structural differences between products C and (21)
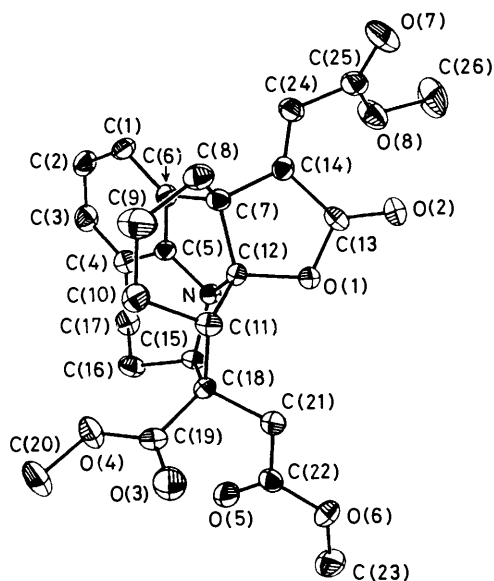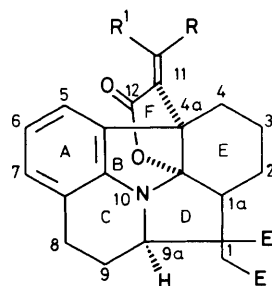
Figure. Perspective view of the (Z)-methyl 1-methoxycarbonyl-methyl-11-methoxycarbonylmethylene-12-oxo-1,1a,1b,2,3,4,4a-8,9,9a-decahydro-1b,4a-epoxyethanoindolizino[2,3,4,5,6-iklm]carbazole-1-carboxylate (21)

(21) R = H, R^1 = E, D/E cis-fused, CH_2E exo-
(22) R = H, R^1 = E, D/E cis-fused, CH_2E endo-
(23) R = H, R^1 = E, D/E trans-fused, CH_2E exo
(24) R = H, R^1 = E, D/E trans-fused, CH_2E endo
(25) R = E, R^1 = H, D/E trans-fused, CH_2E exo
(26) R = E, R^1 = H, D/E cis-fused, CH_2E endo
(27) R = E, R^1 = H, D/E trans-fused, CH_2E endo

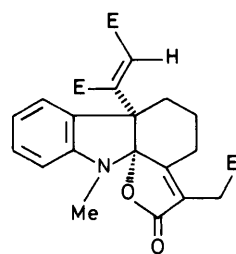

(20)

(35)

(36)

(37)

E = CO_2Me

involve only changes near to or at C-1 of (21). Taking into account the likely mode of formation of (21), and considering possible structural variations consistent with the spectral data, no other differences apart from stereochemical ones seem probable. Thus two positions of possible stereochemical difference exist with respect to the newly formed ring D. (i) The D/E ring junction may be cis- [as in (21)] or trans-fused. The former involving cis-addition of water to the enamine (33), and the latter a trans-addition. (ii) The cyclisation step could yield either an endo- or exo-CH_2E group. Considering cyclisation via a 1,5-dipole, the former would result from the (Z)-form of (31) and the latter from the (E)-form, as in the formation of (21).

The possibility of trans-fused C/D rings is most unlikely considering the strain shown in Dreiding models. This leads to three possible structures for product C, viz. (22), (23), and (24). Compound D, on the other hand, exhibits a lactone CO less strongly coupled (7.3 Hz) to the olefinic proton, revealing a cis-relationship between these groups. The remaining part of the ^{13}C n.m.r. spectrum is identical with that of compound C to within 1.1 p.p.m. except for three minor differences, viz. (C signal/D signal) δ 29.5/26.8 for a CH_2 group, δ 120.4/124.2 for the olefinic proton-bearing carbon, and δ 140.3/145.1 p.p.m. for an sp^2 carbon. Similar differences exist between the geometrical isomers (9) and (10) which also possess the γ-lactone moiety, suggesting that the only difference between C and D is in the geometrical isomerism of the exocyclic double bond. Consequently compound D is considered to be one of the following stereo-isomers, (25), (26), or (27).
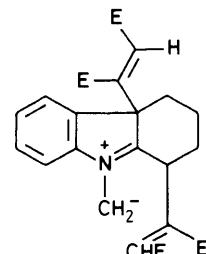
Compound F, formed by the addition of three moles of DMAD to the indole (5) gives spectra revealing the presence of six ester groups, two similar olefinic protons, and from the ^{13}C n.m.r. multiplicities (Table 2) an indication that simple electrophilic addition at two sites in the molecule has occurred. A comparison of ^1H n.m.r. resonances of the olefinic signals of compound F (singlets at δ 6.1 and 6.0), with those of a (1 + 1 DMAD) adduct (36) [9] which has a 3-maleate side chain (olefinic ^1H at δ 6.10), and some (1 + 2 DMAD) adducts [e.g. (37)] [9] which have two maleate side chains (with olefinic protons at δ 6.1 and 5.4), reduces the number of
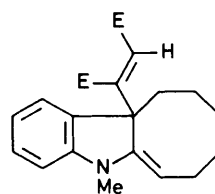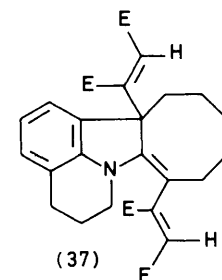
probable structures to two, either (38) or (39). Their formation may be rationalised as in Scheme 3, with the latter having a hypothetical cyclobutene [1] [either (40) or (41)] as an intermediate.

These results show that all N-methyl-[2] and pyridoindoles [(1), (2), (4), and (5)] having either a tri- or a tetra-methylene chain joining positions 2 and 3 react by initial attack of DMAD at the 3-position leading to a similar array of (1 + 1 DMAD − CH_2) lactones or derivatives. Several other compounds with quite different structures were also isolated, which reflect the small steric and proximity differences present in the intermediates. Thus the carbazoles (2) [2] and (5) [also (3) [3]] readily form triones [e.g. (17)] in wet acetic acid, and the tetracyclic carbazole (5) gives mainly the hexacyclic (1 + 2 DMAD − CH_2) lactones [e.g. (21)] from wet methanol or acetonitrile. The N-methylcarbazole (2) does not form such lactones [apparently the zwitterion (35) is not as stable as the postulated (30)], but it does give a less complex tetracyclic (1 + 2 DMAD − CH_2) lactone (20).[2,5] The cyclopentenes (1) and (4)

(5)
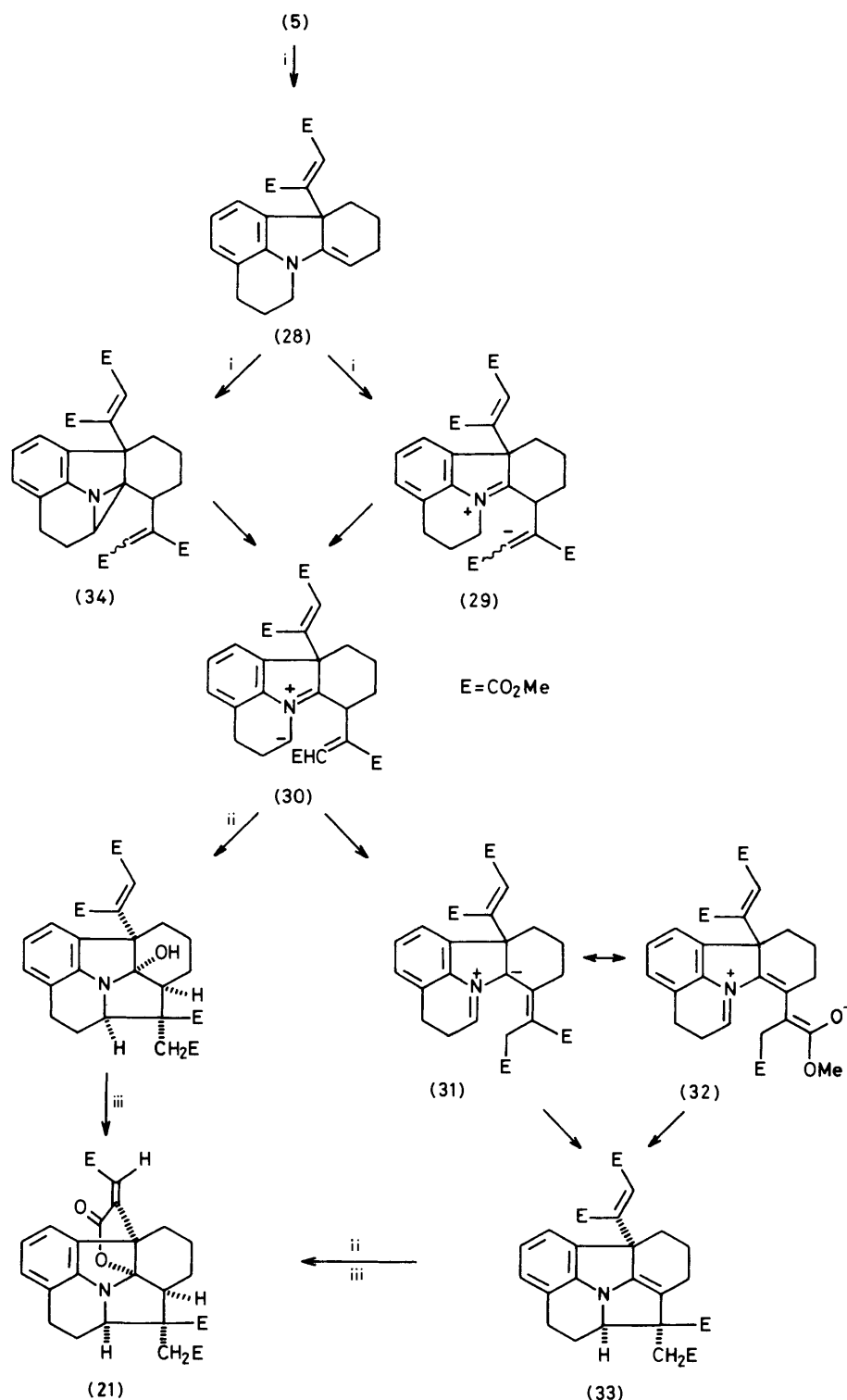
Scheme 2. *Reagents*: i, EC≡CE; ii, H₂O; iii, —MeOH

both give the ring-opened 1-benzazocin-2-ones in wet acetonitrile, no doubt as a result of the greater steric strain present in their reaction intermediates, when compared with the cyclohexenes (2) and (5).

Experimental

The instruments and procedures are given in refs. 1 and 4.

Preparation of Indoles.—Reaction of 1-amino-1,2,3,4-tetrahydroquinoline [1] with a ketone followed by hydrolysis [1] gave the corresponding indole as follows. Cyclopentanone gave 5,6,9,10-*tetrahydro*-4H,8H-*cyclopenta*[4,5]*pyrrolo*[3,2,1-ij]-*quinoline* (4) (70%), m.p. 37—38 °C (from methanol) (Found: C, 85.2; H, 7.8; N, 7.1. $C_{14}H_{15}N$ requires C, 85.2; H, 7.7; N, 7.1%); $\lambda_{max.}$ 233 (ε 24 000) and 285 nm (7 230); m/z 197 (M^+, 100%); δ 7.3—6.7 (3 H, m), 2.98 (2 H, t, J 7 Hz), and 3.0—

E = CO₂Me
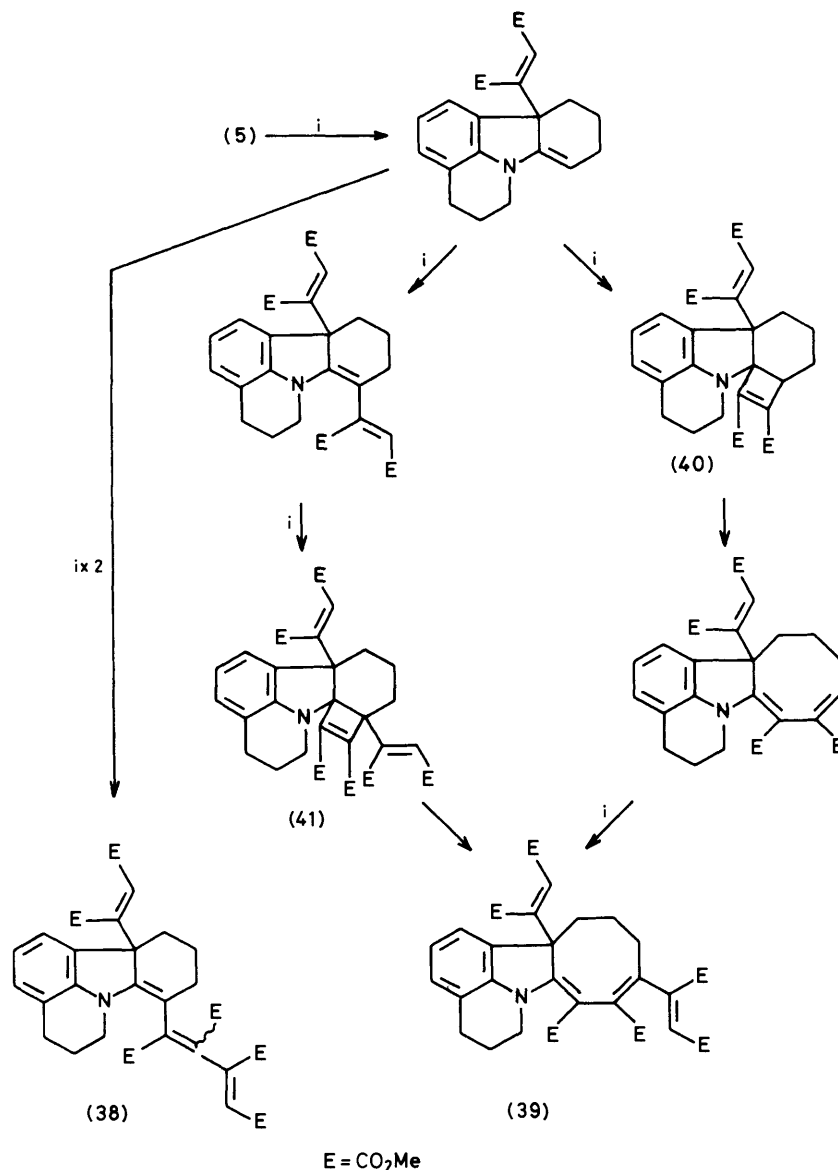
Scheme 3. *Reagents*: i, DMAD

2.0 (10 H, m); cyclohexanone gave 5,6,8,9,10,11-hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole (5), m.p. 65—66 °C (lit.,[10] m.p. 65 °C).

The Indole (4) *and Dimethyl Acetylenedicarboxylate.*—The indole (4) (1 g) and DMAD (2 g) were kept for 2 days in either refluxing 95% aqueous methanol (60 ml) or 98% acetic acid (40 ml) at 100 °C, and then evaporated and t.l.c. (chloroform) carried out. Crystalline products were obtained from two bands. (i) The orange band (R_F 0.8) gave orange prisms (0.3 g) (from ethanol) of (E)-*methyl* 9-*oxo*-5,6,7a,9,10,10a-*hexahydro*-4*H*-7a,10a-*propanofuro*[3',2':4,5]*pyrrolo*[3,2,1-*ij*]-*quinolin*-10-*ylideneacetate* (6), m.p. 110—110.5 °C (Found: C, 70.3; H, 6.0; N, 4.5. $C_{19}H_{19}NO_4$ requires C, 70.15; H, 5.9; N, 4.3%); $v_{max.}$ 1 755s and 1 731s cm⁻¹; $\lambda_{max.}$ 235 (ε 13 600) and 297 nm (2 900); *m/z* 325 (M^+, 100%), 294 (12), 266 (18), and 222 (18); δ 7.38 (1 H, d, *J* 5.8 Hz, 1-H) 7.0—6.4 (2 H, m, 2-, 3-H), 6.79 (1 H, s, olefinic H), 3.85 (3 H, s, OMe), and 3.5—1.5 (12 H, m, aliphatic H). (ii) The yellow band (R_F 0.4) gave yellow needles (0.35 g) (from ethanol) of (Z)-*methyl* 9-*oxo*-

5,6,7a,9,10,10a-*hexahydro*-4*H*-7a,10a-*propanofuro*[3',2':4,5]-*pyrrolo*[3,2,1-*ij*]*quinolin*-10-*ylideneacetate* (7), m.p. 183—184 °C (Found: C, 70.15; H, 5.9; N, 4.5. $C_{19}H_{19}NO_4$ requires C, 70.15; H, 5.9; N, 4.3%); $v_{max.}$ 1 736s cm⁻¹; $\lambda_{max.}$ 250 (ε 8 700) and 301 nm (1 600); *m/z* 325 (M^+, 100%), 250 (25), 238 (25), and 224 (45); δ 7.0—6.6 (3 H, m, aryl H), 6.52 (1 H, s, olefinic H), 3.80 (3 H, s, OMe), 3.2—2.5 (2 H, m, CH_2N), and 2.5—1.7 (10 H, m, aliphatic H).

The indole (4) (1 g) and DMAD (2 g) in 98% aqueous acetonitrile (50 ml) were refluxed for 4 days and then evaporated and t.l.c. (chloroform) carried out. Crystalline products were obtained from two bands. (i) The yellow band (R_F 0.4) gave compound (7) (0.5 g). (ii) The pale orange band which appeared dark blue under u.v.₂₅₄ light (R_F 0.3) gave colourless plates (0.12 g) of a product A, dimethyl 8-*oxo*-5,6,9,10,-11,12-*hexahydro*-4*H*,8*H*-*azocino*[3,2,1-*ij*]*quinolin*-12-*ylidene*-*succinate* (11) or (12), m.p. 144—145 °C (Found: C, 67.3; H, 6.3; N, 3.9. $C_{20}H_{23}NO_5$ requires C, 67.2; H, 6.5; N, 3.9%); $v_{max.}$ 1 740s, 1 716s, and 1 643s cm⁻¹; $\lambda_{max.}$ 216 (ε 22 500) and 235 nm (14 400); *m/z* 357 (M^+, 100%), 329 (70), 326 (35), 298

Table 4. Bond lengths (Å), bond angles (°), and torsion angles (°) for compound (21)

C(1)–C(2)	1.395(5)	C(1)–C(6)	1.390(5)
C(2)–C(3)	1.383(5)	C(3)–C(4)	1.390(6)
C(4)–C(5)	1.380(5)	C(4)–C(17)	1.509(4)
C(5)–C(6)	1.379(4)	C(5)–N	1.409(5)
C(6)–C(7)	1.518(5)	C(7)–C(8)	1.535(5)
C(7)–C(12)	1.565(4)	C(7)–C(14)	1.513(5)
C(8)–C(9)	1.530(5)	C(9)–C(10)	1.538(5)
C(10)–C(11)	1.536(5)	C(11)–C(12)	1.525(5)
C(11)–C(18)	1.568(4)	C(12)–N	1.446(4)
C(12)–O(1)	1.458(4)	C(13)–C(14)	1.488(5)
C(13)–O(1)	1.361(4)	C(13)–O(2)	1.203(4)
C(14)–C(24)	1.321(5)	C(15)–C(16)	1.540(5)
C(15)–C(18)	1.593(5)	C(15)–N	1.479(4)
C(16)–C(17)	1.543(5)	C(18)–C(19)	1.528(5)
C(18)–C(21)	1.545(5)	C(19)–O(3)	1.199(5)
C(19)–O(4)	1.323(5)	C(20)–O(4)	1.442(5)
C(21)–C(22)	1.497(5)	C(22)–O(5)	1.209(5)
C(22)–O(6)	1.337(5)	C(23)–O(6)	1.447(4)
C(24)–C(25)	1.493(5)	C(25)–O(7)	1.201(4)
C(25)–O(8)	1.326(5)	C(26)–O(8)	1.457(6)
C(2)–C(1)–C(6)	117.9(3)	C(1)–C(2)–C(3)	121.7(4)
C(2)–C(3)–C(4)	120.8(4)	C(3)–C(4)–C(5)	116.3(3)
C(3)–C(4)–C(17)	128.4(3)	C(5)–C(4)–C(17)	114.7(3)
C(4)–C(5)–C(6)	124.3(3)	C(4)–C(5)–N	123.1(3)
C(6)–C(5)–N	112.6(3)	C(1)–C(6)–C(5)	118.9(3)
C(1)–C(6)–C(7)	132.4(3)	C(5)–C(6)–C(7)	108.6(3)
C(6)–C(7)–C(8)	117.0(3)	C(6)–C(7)–C(12)	101.9(2)
C(8)–C(7)–C(12)	110.5(3)	C(6)–C(7)–C(14)	113.5(3)
C(8)–C(7)–C(14)	110.7(3)	C(12)–C(7)–C(14)	101.8(3)
C(7)–C(8)–C(9)	113.2(3)	C(8)–C(9)–C(10)	114.8(3)
C(9)–C(10)–C(11)	113.3(3)	C(10)–C(11)–C(12)	108.5(3)
C(10)–C(11)–C(18)	113.6(3)	C(12)–C(11)–C(18)	103.3(3)
C(7)–C(12)–C(11)	118.3(3)	C(7)–C(12)–N	106.2(3)
C(11)–C(12)–N	105.2(2)	C(7)–C(12)–O(1)	106.1(2)
C(11)–C(12)–O(1)	109.6(3)	N–C(12)–O(1)	111.4(3)
C(14)–C(13)–O(1)	109.2(3)	C(14)–C(13)–O(2)	129.3(3)
O(1)–C(13)–O(2)	121.5(3)	C(7)–C(14)–C(13)	107.7(3)
C(7)–C(14)–C(24)	127.7(3)	C(13)–C(14)–C(24)	124.6(3)
C(16)–C(15)–C(18)	121.1(3)	C(16)–C(15)–N	111.1(3)
C(18)–C(15)–N	103.9(2)	C(15)–C(16)–C(17)	111.3(3)
C(4)–C(17)–C(16)	106.8(3)	C(11)–C(18)–C(15)	103.8(3)
C(11)–C(18)–C(19)	108.9(3)	C(15)–C(18)–C(19)	120.7(3)
C(11)–C(18)–C(21)	109.4(3)	C(15)–C(18)–C(21)	107.6(3)
C(19)–C(18)–C(21)	106.1(3)	C(18)–C(19)–O(3)	121.3(4)
C(18)–C(19)–O(4)	116.0(3)	O(3)–C(19)–O(4)	122.6(3)
C(18)–C(21)–C(22)	112.8(3)	C(21)–C(22)–O(5)	125.6(4)
C(21)–C(22)–O(6)	111.0(3)	O(5)–C(22)–O(6)	123.4(3)
C(14)–C(24)–C(25)	124.7(4)	C(24)–C(25)–O(7)	123.1(4)
C(24)–C(25)–O(8)	112.0(3)	O(7)–C(25)–O(8)	124.8(4)
C(5)–N–C(12)	107.5(2)	C(5)–N–C(15)	118.5(3)
C(12)–N–C(15)	112.5(3)	C(12)–O(1)–C(13)	111.7(3)
C(19)–O(4)–C(20)	116.1(3)	C(22)–O(6)–C(23)	116.3(3)
C(25)–O(8)–C(26)	115.8(3)		
C(5)–C(6)–C(7)–C(12)	−9.2(4)	C(7)–C(12)–O(1)–C(13)	−12.1(3)
C(6)–C(7)–C(12)–N	16.5(3)	C(12)–O(1)–C(13)–C(14)	0.7(3)
C(7)–C(12)–N–C(5)	−18.2(3)	O(1)–C(13)–C(14)–C(7)	11.5(4)
C(12)–N–C(5)–C(6)	12.9(4)	C(13)–C(14)–C(7)–C(12)	−17.6(3)
N–C(5)–C(6)–C(7)	−1.6(4)	C(14)–C(7)–C(12)–O(1)	17.8(3)
C(5)–N–C(15)–C(16)	9.5(4)	C(7)–C(8)–C(9)–C(10)	27.0(5)
N–C(15)–C(16)–C(17)	38.0(4)	C(8)–C(9)–C(10)–C(11)	30.7(5)
C(15)–C(16)–C(17)–C(4)	−63.8(4)	C(9)–C(10)–C(11)–C(12)	−59.3(4)
C(16)–C(17)–C(4)–C(5)	41.8(4)	C(10)–C(11)–C(12)–C(7)	30.8(4)
C(17)–C(4)–C(5)–N	5.5(5)	C(11)–C(12)–C(7)–C(8)	23.7(4)
C(4)–C(5)–N–C(15)	−34.4(5)	C(12)–C(7)–C(8)–C(9)	−53.8(4)

Table 5. Fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses for compound (21)

Atom	x	y	z	U_{eq} *
C(1)	$-205(5)$	2 535(3)	2 950(2)	38(1)
C(2)	495(6)	2 558(4)	3 796(3)	44(2)
C(3)	1 632(5)	3 600(4)	4 307(2)	44(2)
C(4)	2 178(5)	4 649(3)	3 982(2)	33(1)
C(5)	1 499(5)	4 591(3)	3 138(2)	30(1)
C(6)	303(5)	3 590(3)	2 623(2)	31(1)
C(7)	$-281(5)$	3 938(3)	1 773(2)	28(1)
C(8)	$-2 433(5)$	3 804(3)	1 456(2)	40(1)
C(9)	$-3 620(5)$	4 695(4)	2 061(3)	60(2)
C(10)	$-2 516(5)$	5 942(3)	2 607(2)	41(2)
C(11)	$-909(5)$	6 443(3)	2 160(2)	31(1)
C(12)	504(5)	5 389(3)	1 962(2)	27(1)
C(13)	1 682(5)	4 349(3)	693(2)	34(1)
C(14)	867(5)	3 306(3)	1 060(2)	30(1)
C(15)	1 979(5)	6 954(3)	3 239(2)	30(1)
C(16)	2 001(5)	7 002(3)	4 204(2)	38(1)
C(17)	3 189(5)	5 931(3)	4 461(2)	43(2)
C(18)	370(5)	7 620(3)	2 749(2)	28(1)
C(19)	$-926(5)$	8 566(4)	3 252(2)	36(1)
C(20)	$-2 611(6)$	9 195(4)	4 453(3)	57(2)
C(21)	1 378(5)	8 373(3)	2 182(2)	34(1)
C(22)	2 589(5)	9 539(3)	2 697(3)	36(1)
C(23)	4 537(6)	11 364(4)	2 605(3)	56(2)
C(24)	1 119(5)	2 058(3)	788(2)	38(1)
C(25)	2 180(6)	1 494(3)	44(2)	44(2)
C(26)	5 158(7)	1 464(5)	$-522(3)$	87(3)
N	1 863(4)	5 600(2)	2 726(2)	26(1)
O(1)	1 446(3)	5 523(2)	1 215(1)	31(1)
O(2)	2 411(4)	4 260(2)	38(1)	49(1)
O(3)	$-1 690(4)$	9 370(3)	2 944(2)	65(1)
O(4)	$-1 254(4)$	8 380(2)	4 012(2)	46(1)
O(5)	2 946(4)	9 820(2)	3 471(2)	48(1)
O(6)	3 250(4)	10 249(2)	2 187(2)	47(1)
O(7)	1 420(4)	780(3)	$-605(2)$	65(1)
O(8)	4 043(4)	1 836(3)	203(2)	60(1)

* U_{eq} is the equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

(46), and 270 (80); δ 7.3—6.7 (3 H, m, aryl H), 4.38 (2 H, m, NCH₂), 3.74 (3 H, s, OMe), 3.57 (3 H, s, OMe), 2.81 (2 H, s, CH₂), and 3.4—1.2 (10 H, m, 5 × CH₂).

Reaction of the Indole (1) *and Dimethyl Acetylenedicarboxylate.*—The indole (1)[2] (1 g) and DMAD (2 g) in 98% aqueous acetonitrile (40 ml) were refluxed for 4 days and then evaporated and t.l.c. (chloroform) carried out. Crystalline products were obtained from two bands. (i) The yellow band (R_F 0.4) gave yellow lathes (0.4 g) of compound (16).[2] (ii) The pale orange band (R_F 0.3) which appeared dark blue under u.v.₂₅₄ light gave colourless plates (0.12 g) of product B, *dimethyl 1-methyl-2-oxo-1,2,3,4,5,6-hexahydro-1-benzazocin-6-ylidene-succinate* (13) or (14), m.p. 151—152 °C (Found: C, 65.0; H, 6.4; N, 4.3. C₁₈H₂₁NO₅ requires C, 65.25; H, 6.4; N, 4.2%); $\nu_{max.}$ 1 737s, 1 715m, and 1 635s cm⁻¹; $\lambda_{max.}$ 212 (ε 15 000) and 220 nm (14 100); m/z 331 (M^+, 100%), 303 (20), 300 (40), 272 (33), and 244 (55); δ 7.5—6.9 (4 H, m, aryl H), 3.75 (3 H, s, OMe), 3.60 (3 H, s, OMe), 3.23 (3 H, s, NMe), 2.96 (2 H, s, CH₂), and 2.5—1.5 (6 H, m, 3 × CH₂).

Reaction of the Indole (5) *and Dimethyl Acetylenedicarboxylate.*—The indole (5) (1 g) and DMAD (2 g) in 98% aqueous acetic acid (50 ml) were kept at 100 °C for 5 days and then evaporated and t.l.c. (chloroform–ethyl acetate, 19 : 1 v/v) carried out. Crystalline products were obtained from two bands. (i) The yellow band (R_F 0.6) gave yellow needles (0.36 g)

(from ethanol) of 5,6,12,13,14,14a-*hexahydro*-4H,11H-11,14a-*methanocyclo-octa*[c]*pyrido*[3,2,1-ij]*quinoline*-8,10,15-*trione* (17), m.p. 220—221 °C (Found: C, 74.6; H, 5.8; N, 4.6. C₁₉H₁₇NO₃ requires C, 74.3; H, 5.6; N, 4.6%); $\nu_{max.}$ 1 736s, 1 673s, and 1 650s cm⁻¹; $\lambda_{max.}$ 236.5 (ε 10 800), 251.5 (5 600), 281 (2 200), 290 (2 100), and 334 nm (2 400); m/z 307 (M^+, 46%), 242 (58), and 213 (100); δ 7.56—6.9 (4 H, m) and 4.5—1.4 (13 H, m). (ii) The pale brown band (R_F 0.1) gave yellow needles (45 mg) (from ethanol–ether) of (Z)-9-*oxo*-5,6,7a,9,10,10a-*hexahydro*-4H-7a,10a-*butanofuro*[3′,2′:4,5]*pyrrolo*-[3,2,1-ij]*quinolin*-10-*ylideneacetic acid* (8), m.p. 168—169 °C (Found: C, 70.0; H, 5.5; N, 3.9. C₁₉H₁₉NO₄ requires C, 70.15; H, 5.9; N, 4.3%); $\nu_{max.}$ 3 050—2 500w, 1 720s, and 1 710s cm⁻¹; $\lambda_{max.}$ 241 (ε 10 300) and 298 nm (800); m/z 325 (M^+, 100%), 281 (62), and 236 (70). Rapid treatment with an excess of diazomethane gave pale yellow needles of (Z)-*methyl* 9-*oxo*-5,6,7a,9,10,10a-*hexahydro*-4H-7a,10a-*butanofuro*[3′,2′:4,5]-*pyrrolo*[3,2,1-ij]*quinolin*-10-*ylideneacetate* (9) (from ethanol), m.p. 179—180 °C (Found: C, 70.6; H, 6.4; N, 4.3. C₂₀H₂₁NO₄ requires C, 70.8; H, 6.25; N, 4.15%; $\nu_{max.}$ 1 739s cm⁻¹; $\lambda_{max.}$ 241 (ε 9 600) and 298 nm (1 200); m/z 339 (M^+, 100%), 295 (42), 280 (30), and 236 (83); δ 7.1—6.6 (3 H, m, aryl H), 6.41 (1 H, s, olefinic H), 3.84 (3 H, s, OMe), and 3.75—1.1 (14 H, m, aliphatic H).

The indole (5) (1 g) was refluxed with DMAD (2 g) for 4 days in water–methanol (1 : 9 v/v) (50 ml) and the mixture then evaporated and t.l.c. (chloroform) carried out. Apart from the carbazole (5) (0.1 g), crystalline products were obtained from four bands. (i) The yellow band (R_F 0.8) gave yellow needles (0.15 g) (from ethanol) of (E)-*methyl* 9-*oxo*-5,6,7a,9,10,10a-*hexahydro*-4H-7a,10a-*butanofuro*[3′,2′:4,5]-*pyrrolo*[3,2,1-ij]*quinolin*-10-*ylideneacetate* (10), m.p. 116—117 °C (Found: C, 70.8; H, 6.0; N, 4.3. C₂₀H₂₁NO₄ requires C, 70.8; H, 6.25; N, 4.15%); $\nu_{max.}$ 1 760 (s) and 1 728 cm⁻¹ (s); $\lambda_{max.}$ 238 (ε 15 000) and 280 nm (2 500); m/z 339 (M^+, 100%), 295 (24), 280 (15), 230 (57), and 221 (30); δ 7.32 (1 H, d, J 7.0 Hz, 1-H), 6.95 (1 H, s, olefinic H), 6.91 (1 H, d, J 7.0 Hz, 3-H), 6.67 (1 H, t, J 7.0 Hz, 2-H), 3.87 (3 H, s, OMe), and 3.6—1.0 (14 H, m, aliphatic H). (ii) The yellow band (R_F 0.7) gave pale yellow lathes (0.1 g) (from ethanol) of *methyl* 9-*oxo*-5,6,7a,11a-*tetrahydro*-4H,9H-7a,11a-*butanopyrano*-[3′,2′:4,5]*pyrrolo*[3,2,1-ij]*quinoline*-11-*carboxylate* (19), m.p. 145—146 °C (Found: C, 71.0; H, 6.05; N, 4.0. C₂₀H₂₁NO₄ requires C, 70.8; H, 6.25; N, 4.15%); $\nu_{max.}$ 1 720 (s) cm⁻¹; $\lambda_{max.}$ 220 nm (ε 11 000) and 285 (4 000); m/z 339 (M^+, 100%), 295 (19), 236 (22), and 211 (66); δ 7.23 (1 H, d, J 7.0 Hz, 1-H), 6.87 (1 H, t, J 7.0 Hz, 2-H), 6.74 (1 H, d, J 7.0 Hz, 3-H), 6.64 (1 H, s, olefinic H), 3.87 (3 H, s, OMe), and 3.6—1.0 (14 H, m, aliphatic H). (iii) The pale yellow band (R_F 0.3) gave pale yellow plates (0.43 g) (from ethanol) of product D, (E)-*methyl* 1-*methoxycarbonylmethyl*-11-*methoxycarbonylmethylene*-12-*oxo*-1,1a,1b,2,3,4,4a,8,9,9a-*decahydro*-1b,4a-*epoxyethanoindolizino*[2,3,4,5,6-jklm]*carbazole*-1-*carboxylate* (25), (26), or (27), m.p. 236—237 °C (Found: C, 65.05; H, 5.65; N, 2.8. C₂₆H₂₇NO₈ requires C, 64.85; H, 5.65; N, 2.9%); $\nu_{max.}$ 1 771 (s), 1 745 (m), and 1 731 cm⁻¹ (s); $\lambda_{max.}$ 237 (ε 12 000), and 294 nm (2 600); m/z 481 (M^+, 100%), 450 (20), 422 (38), and 408 (25); δ 7.43 (1 H, d, J 6.6 Hz, 5-H), 6.90 (1 H, d, J 6.6 Hz, 7-H), 6.67 (1 H, t, J 6.6 Hz, 6-H), 6.82 (1 H, s, olefinic H), 4.90 (1 H, dd, J 10.9, 5.7 Hz, 9a-H), 3.86 (3 H, s, OMe), 3.80 (3 H, s, OMe), 3.70 (3 H, s, OMe), 2.97 (1 H, d, J 16.5 Hz, CHHE), 2.54 (1 H, d, J 16.5, CHHE), and 3.2—0.4 (11 H, m, aliphatic H). (iv) The pale yellow band (R_F 0.2) gave colourless prisms (0.30 g) (from ethanol) of product C, (Z)-*methyl* 1-*methoxycarbonylmethyl*-11-*methoxycarbonyl-methylene*-12-*oxo*-1,1a,1b,2,3,4,4a,8,9,9a-*decahydro*-1b,4a-*epoxyethanoindolizino*[2,3,4,5,6-jklm]*carbazole*-1-*carboxylate* (22), (23), or (24), m.p. 177—178 °C (Found: C, 65.0; H,

5.66; N, 3.2. $C_{26}H_{27}NO_8$ requires C, 64.85; H, 5.65; N, 2.9%); $\nu_{max.}$ 1 770 (s), 1 750 (m), and 1 729 cm^{-1} (s); $\lambda_{max.}$ 243 (ε 9 700) and 291.5 nm (2 300); m/z 481 (M^+, 100%), 450 (22), 422 (40), and 408 (20); δ 7.1–6.7 (3 H, m, aryl H), 6.37 (1 H, s, olefinic H), 4.90 (1 H, dd, J 11.8, 6.1 Hz, 9a-H), 3.84 (3 H, s. OMe), 3.77 (3 H, s, OMe), 3.66 (3 H, s, OMe), 2.98 (1 H, d, J 16.8 Hz, CHHE), 2.52 (1 H, d, J 16.8 Hz, CHHE), and 2.7—0.6 (11 H, m, aliphatic H).

The indole (5) (1 g) was refluxed with DMAD (2 g) for 4 days in water–methanol (1 : 49 v/v) (50 ml) and the mixture then evaporated and t.l.c. (chloroform) carried out. Apart from compound (5) (0.2 g), crystalline products were obtained from two bands. (i) The pale yellow band (R_F 0.3) gave pale yellow plates (0.45 g) (from ethanol) of product C [(22), (23), or (24)]. (ii) The pale yellow band (R_F 0.2) gave colourless prisms (0.23 g) (from ethanol) of product D [(25), (26), or (27)].

The indole (5) (1 g) and DMAD (2 g) in water–acetonitrile (1 : 49 v/v) (50 ml) were kept at 100 °C for 4 days and the mixture was then evaporated and t.l.c. (chloroform) carried out. Apart from (5) (0.15 g), crystalline products were obtained from three bands. (i) The yellow band (R_F 0.7) gave pale yellow lathes (0.1 g) (from ethanol) of the pyrano-compound (19). (ii) The pale yellow band (R_F 0.6) gave pale yellow prisms (0.43 g) (from ethanol) of (Z)-*methyl* 1-*methoxy-carbonylmethyl*-11-*methoxycarbonylmethylene*-12-*oxo*-1,1a,1b,2,3,4,4a,8,9,9a-*decahydro*-1b,4a-*epoxyethanoindolizino*[2,3,4,5,6-jklm]*carbazole*-1-*carboxylate* (21), m.p. 165—166 °C (Found: C, 64.7; H, 5.7; N, 2.8. $C_{26}H_{27}NO_8$ requires C, 64.85; H, 5.65; N, 2.9%); $\nu_{max.}$ 1 752 (s) and 1 730 cm^{-1} (s); $\lambda_{max.}$ 236 (ε 13 000) and 288 nm (2 290); m/z 481 (M^+, 100%), 450 (22), 422 (28), 409 (20), and 407 (20); δ 7.1—6.5 (3 H, m, aryl H), 6.48 (1 H, s, olefinic H), 3.97 (1 H, dd, J 10.5, 7.0 Hz, 9a-H), 3.79 (3 H, s, OMe), 3.69 (3 H, s, OMe), 3.43 (3 H, s, OMe), 3.15 (2 H, s, CH$_2$), and 2.9—0.8 (11 H, m, aliphatic H). (iii) The golden yellow band (R_F 0.05) gave yellow prisms (0.15 g) (from chloroform–ethanol) of product F, (38) or (39), m.p. 180—181 °C (Found: C, 62.0; H, 5.55; N, 2.25. $C_{33}H_{35}NO_{12}$ requires C, 62.2; H, 5.5; N, 2.2%); $\nu_{max.}$ 1 730 (s) and 1 720 cm^{-1} (s); $\lambda_{max.}$ 211 (ε 22 400); 248 (shoulder) (10 900), 336 (9 400), and 406 nm (11 000); m/z 637 (M^+, 90%) and 578 (100); δ 7.28—6.8 (3 H, m, aryl H), 6.13 (1 H, s, olefinic H), 6.06 (1 H, s, olefinic H), 3.84 (3 H, s, OMe), 3.76 (6 H, s, 2 × OMe), 3.68 (9 H, s, 3 × OMe), and 4.2—1.0 (12 H, m, aliphatic H).

The indole (5) (0.8 g) was refluxed with DMAD (2 g) for 3 days in water–acetonitrile (3 : 17 v/v) (50 ml) and yielded the following products from t.l.c. (chloroform): (i) compound (19) (0.24 g) from the band at R_F 0.7; (ii) product E, (21) (0.25 g) from the band at R_F 0.6; (iii) product C, (22), (23), or (24) (0.15 g) from the band at R_F 0.3; (iv) product D, (25), (26), or (27) (0.14 g) from the band at R_F 0.2.

X-*Ray Crystal Structure Analysis of Compound* (21).—A needle-shaped single crystal of dimensions 0.2 × 0.3 × 0.5 mm was used for the diffraction measurements.

Crystal Data.—$C_{26}H_{27}NO_8$, $M = 481.51$, triclinic, $a = 7.016(1)$, $b = 10.611(2)$, $c = 16.083(5)$ Å, $\alpha = 103.26(2)$, $\beta = 95.71(2)$, $\gamma = 92.38(2)°$, $U = 1$ 157 Å^3, $D_m = 1.40$ g cm^{-3},

$Z = 2$, $D_c = 1.382$ g cm^{-3}, space group $P\bar{1}$ (from intensity statistics), Mo-K_α radiation (graphite-monochromatised), $\lambda = 0.710$ 69 Å, μ(Mo-K_α) = 0.96 cm^{-1}.

Unit-cell dimensions were determined from least-squares refinement of 20 high-angle reflections measured on a Nicolet R3m diffractometer. Intensities were measured using the $\theta - 2\theta$ scan technique, with variable scan speeds from 2 to 8° min^{-1} and a scan range from 1° below the $K_{\alpha 1}$ peak to 1° above the $K_{\alpha 2}$ peak. Background counts were taken for half the scan time at each end of the scan range. Three standard reflections, monitored every 50 intensity measurements, showed only random variations within 2% of their initial values. Of the 5 071 unique reflections recorded in the range 0° < 2θ < 50°, 2 884 for which $|F| > 3\sigma(|F|)$ were considered observed and used in subsequent calculations. The data were corrected for Lorentz and polarization factors but not for absorption and extinction.

The structure was solved by the direct method based on negative quartets,[11] and all non-hydrogen atoms appeared on the best E-map. These were refined anisotropically to $R = 0.091$, and the resulting difference map revealed peaks corresponding to all hydrogen atoms except two belonging to an end methyl group. In the last stage of refinement, the hydrogen atoms were generated and allowed to ride on their respective parent carbon atoms with assigned isotropic thermal parameters. The ' goodness-of-fit ' index, defined as $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, converged to 1.551; in this expression, N_o is the number of observed reflections, and $N_v = 325$, the number of variable parameters. The last least-squares cycle yielded $R = 0.079$, and the final difference map contained no residual peaks higher than 0.36 e Å^{-3}.

All computations were performed with the SHELXTL[12] package of crystallographic programs on a Nova 3 mini-computer. The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(|F|) + 0.001|F|^2]^{-1}$.

The final atomic co-ordinates of the non-hydrogen atoms are given in Table 5 in accordance with the labelling scheme in the Figure. Bond lengths, bond angles, and selected torsion angles are listed in Table 4.*

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* The anisotropic thermal parameters for the non-hydrogen atoms, the positional and thermal parameters for the hydrogen atoms, and observed and calculated structure factors are available as a Supplementary Publication (SUP No. 23493, 21 pages). For details see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.