Addition Reactions of Heterocyclic Compounds. Part 77.[1] Reaction of Dimethyl Acetylenedicarboxylate with 2- and 3-Alkyl Substituted Indoles and the Formation of (1 + 1 DMAD–CH_4O) Adducts

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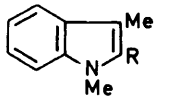
Dimethyl acetylenedicarboxylate (DMAD) adds to 1,3-dimethylindole in moist acetic acid to give 2-substituted adducts. The dienone formulation for a product from 1,2,3-trimethylindole and DMAD has been confirmed by making use of proton-coupled ^{13}C n.m.r. spectra. The generality of the formation of this (1 + 1 DMAD–CH_4O) adduct is shown by the preparation of a further five new dienones including two bicyclo[9,3,1]pentadecadienones.

Addition of dimethyl acetylenedicarboxylate (DMAD) to indole gives many products arising either from initial electrophilic attack at the 3-position (to give a maleate or fumarate [2]) or from cyclisation to a cyclobutene and ring-opening to a benzazepine,[3] and subsequent reactions.[4] 1,2-Dimethylindole yields the 3-maleate and 3-fumarate,[5,6] while 1,3-dimethylindole, which is stated [7] to need boron trifluoride catalysis, gave the 2-maleate, the 2-fumarate, and the corresponding benzazepine. 1,2,3-Trisubstituted indoles, which cannot yield maleates and fumarates, gave,[7] with boron trifluoride–diethyl ether, a benzazepine and another compound (2a), while, in the presence of water, 1-methylindoles possessing a tri-, tetra-, or penta-methylene chain bridging the 2,3-positions yielded [8] a variety of lactones, again formed by initial electrophilic attack of DMAD at the 3-position. In contrast, the strained indole (3a) gave [9] compounds derived from hydrolysis of the initial indole ring, at some stage, to the corresponding amino-ketone.

In order to obtain more information concerning the structural features which promote the various reaction modes outlined above, the addition of DMAD to 1,3-dimethyl- and to 1,2,3-trimethyl-indole, both of which have only been briefly reported,[7] and to a number of other indoles, has been investigated.

DMAD does not need boron trifluoride–diethyl ether catalysis (*cf.* ref. 7) to induce reaction with either 1,3-dimethyl- (1a) or 1,2,3-trimethyl-indole (1b) as both react in refluxing acetic acid containing some water. The dimethylindole gave the maleate (1c) and fumarate (1d) in good yield, together with a small amount of a compound which had lost an ester group and which had two strongly coupled (J 19 Hz) olefinic protons, and must therefore be represented by structure (1e). This compound was also obtained from the indole and methyl propiolate. The ^{13}CO–^1H coupling constants for compounds (1c) and (1d) (Table 1), when compared with the literature values [6] ($^2J_{CO,H} \simeq {}^4J_{CO,H} \simeq 1$ Hz, *trans*-$^3J_{CO,H} \simeq$ 11—14 Hz and *cis*-$^3J_{CO,H} \simeq$ 4—7.5 Hz), confirm the structures proposed.

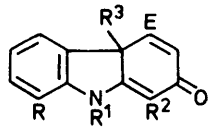
1,2,3-Trimethylindole gave only one product A which was identical in its spectra with one of the compounds obtained [7] using boron trifluoride–diethyl ether; it was assigned structure (2a). Three other structures, (4a), (5a), and (5b), are also consistent with the published spectra.[7] However the proton-coupled ketone carbonyl resonance (δ 183.6 p.p.m.) (Table 2) showed only weak ($J_{CO,H}$ 0.9 Hz) coupling to the high field olefinic proton (δ 5.67). Comparison with the ^1H–^{13}C coupling constant data presented above excludes structures (5a) and (5b), but in order to decide between (2a) and (4a) further



(1)

a; R = H
b; R = Me
c; R = E E
d; R = E E
e; R = E

E = CO_2Me



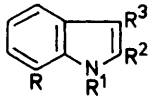
(2)

a; R = R^2 = H, R^1 = R^3 = Me
b; R, R^1 = $(CH_2)_3$, R^2 = H, R^3 = Me
c; R, R^1 = $(CH_2)_3$, R^2 = R^3 = Me
d; R, R^1 = $(CH_2)_3$, R^2 = Et, R^3 = Me
e; R, R^1 = $(CH_2)_3$, R^2, R^3 = $(CH_2)_9$
f; R = H, R^1 = Me, R^2, R^3 = $(CH_2)_9$

comparisons were necessary. Addition of DMAD, under the same conditions, to 1,2-dimethyl- (3c), 2-ethyl-1-methyl- (3d) and 1-methyl-2-n-propyl-5,6-dihydro-4*H*-pyrrolo-[3,2,1-*ij*]quinoline (3e) gave, respectively, compounds B, C, and D with very similar ^1H and ^{13}C (proton-decoupled) n.m.r., i.r., u.v., and mass spectra (Tables 2 and 3) to those of compound A, showing that these compounds all possessed the same basic structure. In the proton-coupled ^{13}C n.m.r. spectra the ketone carbonyl (δ 183.8 p.p.m.) in compound B is a doublet (J 1.0 Hz) coupled to the high-field olefinic proton (δ 5.59) and thus corresponds to the situation for compound A and either structure (2b) or (4b). In structure C the ketone carbonyl (δ 184.1 p.p.m.) is a quartet (J 3.7 Hz) coupled to the methyl signal (δ 2.23) which strongly suggests structure (2c), although the possibility that the angular methyl group of (4c) is the cause cannot be completely excluded even though no coupling with a methyl group is observed for compound A or B. The ketone carbonyl for D is an apparent triplet (J 4.8 Hz) coupled only to the aliphatic resonance at δ 2.80. This is consistent with structure (2d), and not with (4d), and hence compounds A—D must have structures (2a)—(2d) respectively, thus confirming the structure originally assigned to A.[7]

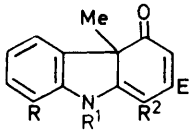
The effect of replacing the two C-alkyl groups in the indoles (1b), (3c), (3d), and (3e) by a decamethylene chain [indoles (3b) and (3f)], has also been examined. In moist acetic acid these 12-membered ring compounds gave, as the only isolable products, (2f) and (2e), respectively, identified from their spectra (Tables 2 and 3).

The new indoles (3b), (3e), and (3f) (see Table 1) employed



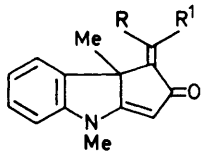
(3)

a; R, R^1 = $(CH_2)_2$, R^2, R^3 = $(CH_2)_4$
b; R = H, R^1 = Me, R^2, R^3 = $(CH_2)_{10}$
c; R, R^1 = $(CH_2)_3$, R^2 = R^3 = Me
d; R, R^1 = $(CH_2)_3$, R^2 = Et, R^3 = Me
e; R, R^1 = $(CH_2)_3$, R^2 = Pr^n, R^3 = Me
f; R, R^1 = $(CH_2)_3$, R^2, R^3 = $(CH_2)_{10}$



(4) E = CO_2Me

a; R = R^2 = H, R^1 = Me
b; R, R^1 = $(CH_2)_3$, R^2 = H
c; R, R^1 = $(CH_2)_3$, R^2 = Me
d; R, R^1 = $(CH_2)_3$, R^2 = Et



(5)

a; R = H, R^1 = E
b; R = E, R^1 = H

in our investigation were synthesised from the corresponding arylhydrazones by Fischer's method, and it is noteworthy that only one, *viz.* (3e), of the two possible indoles was obtained from the arylhydrazone of hexan-3-one.

These reactions show that on the addition of DMAD to 2,3-dialkylindoles formation of dienones, *i.e.* (1 + 1 DMAD–CH_4O) adducts, is a most facile process, also occurring when the alkyl groups are part of a ring which is big enough (12-membered) to overcome the steric factors involved. When the ring is much smaller, thus sterically preventing dienone formation, other reactions have been shown to occur.[8]

These reactions also indicate that there is no difference in the type of reaction product obtained from similarly substituted *N*-methyl- and pyrido[3,2,1-*hi*]indoles, which in the absence of a Lewis acid react with the indole ring intact. This is in contrast to the strained pyrrolo-indole (3a) in which indole ring-opening occurs as it reacts.

Experimental

The instruments and procedures are given in refs. 6 and 8.

Preparation of Indoles.—Using fused zinc chloride, the phenylhydrazones of propionaldehyde and butanone were cyclised to their respective indoles, which on methylation with sodium hydride and methyl iodide yielded, respectively 1,3-dimethylindole (1a) as a colourless oil, b.p. 68—72 °C at 0.05 mmHg (lit.,[10] 119—120 °C at 7 mmHg), δ 7.45—7.25 (1 H, m), 7.15—6.8 (3 H, m), 6.52 (1 H, s), 3.42 (3 H, s), and 2.19 (3 H, s); and 1,2,3-trimethylindole (1b) as a pale yellow oil, b.p. 80—82 °C at 0.01 mmHg (lit.,[10] 283—284 °C at 750 mmHg), δ 7.45—7.2 (1 H, m), 7.1—6.8 (3 H, m), 3.33 (3 H, s), and 2.12 (6 H, s).

Reduction ($LiAlH_4$) of *N*-nitroso-1,2,3,4-tetrahydroquinoline, obtained from 1,2,3,4-tetrahydroquinoline, gave 1-amino-1,2,3,4-tetrahydroquinoline, m.p. 54—55 °C (lit.,[11] m.p. 55 °C). Reaction of this compound with various ketones gave hydrazones which in the presence of 15% sulphuric acid at 100 °C gave the corresponding indoles. In this way butanone gave 1,2-dimethyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (3c), m.p. 87—88 °C (lit.,[11] 87—88 °C); pentan-3-one gave 2-ethyl-1-methyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (3d), m.p. 40 °C (lit.,[11] 39 °C); hexan-3-one gave colourless plates of 1-*methyl*-2-*n*-*propyl*-5,6-*dihydro*-4H-*pyrrolo*[3,2,1-ij]-*quinoline* (3e) (50%), m.p. 50—51 °C (from ethanol) (Found: C, 84.8; H, 9.0; N, 6.8. $C_{15}H_{19}N$ requires C, 84.5; H, 9.0; N, 6.6%), $\lambda_{max.}$ 210 infl. (ε 11 250), 232 (25 000), and 287 nm (7 000); *m*/*z* 213 (M^+, 100%), 197 (60), and 183 (95); δ 7.4—6.7 (3 H, m), 4.0 (2 H, t, *J* 5.5 Hz), 3.0—2.0 (6 H, m), 2.3 (3 H, s), 1.8—1.4 (2 H, m), and 1.0 (3 H, t, *J* 7, 2 Hz); cyclododecanone gave white needles of 5,6,8,9,10,11,12,13,14,15,16,-17-*dodecahydro*-4H-*cyclododeca*[4,5]*pyrrolo*[3,2,1-ij]*quinoline* (3f) (70%), m.p. 134—135 °C (from ethanol) (Found: C, 85.2; H, 9.9; N, 4.6. $C_{21}H_{29}N$ requires C, 85.4; H, 9.9; N, 4.7%), $\lambda_{max.}$ 212 infl. (ε 8 100), 231 (20 600), and 285 nm (4 900); *m*/*z* 295 (M^+, 100%); δ 7.5—6.8 (3 H, m), 4.0 (2 H, t, *J* 6.0 Hz), and 3.1—1.0 (24 H, m).

Reaction of cyclododecanone, with 1-methyl-1-phenylhydrazine, followed by cyclisation with 18% sulphuric acid at 100 °C, gave 5-*methyl*-6,7,8,9,10,11,12,13,14,15-*decahydro*-5H-*cyclododec*[b]*indole* (3b) as white plates, m.p. 84—85 °C (from methanol) (Found: C, 84.9; H, 10.1; N, 5.0. $C_{19}H_{27}N$ requires C, 84.7; H, 10.1; N, 5.2%); $\lambda_{max.}$ 211 infl. (ε 12 000), 231 (26 100), and 285 nm (5 850); *m*/*z* 259 (M^+, 100%) and 245 (75); δ 7.6—7.0 (4 H, m), 3.7 (3 H, s), 2.8—2.7 (4 H, m), and 1.9—1.3 (16 H, m).

Table 1. ^{13}C N.m.r. spectra for solutions in $CDCl_3$ measured at 22.63 MHz and recorded for δ values from tetramethylsilane as internal standard. The multiplicities observed on off-resonance decoupling are noted

Assignment	Compounds				
	(1c)	(1d)	(3b)	(3e)	(3f)
Ester CO	167.0s [a]	165.8s [c]			
	165.0s [b]	164.7s [d]			
sp^2–C	138.9s	137.4s	137.3s	135.7s	135.9s
	138.4s	134.7s	137.1s	126.4s	134.2s
	130.8s	129.1s	127.9s	120.8s	125.8s
	128.1s	127.9s	112.1s	119.0s	120.6s
	113.7s	110.9s	108.5s	106.1s	111.7s
sp^2–CH	125.3d	133.3d	120.6d	118.6d	118.6d
	123.6d	122.1d	118.7d	117.5d	117.7d
	119.7d	119.1d	118.5d	115.4d	116.2d
	119.7d	118.8d			
	109.5d	109.0d			
OMe	52.7q	52.7q			
	52.1q	51.8q			
NMe	31.2q	30.3q	29.8q		
CMe	9.5q	9.1q			
sp^3–CH_2			28.2t	41.7t	42.0t
			27.4t	26.2t	29.7t
			25.4t	24.9t	28.2t
			25.2t	23.1t	27.2t
			24.8t	17.8t	25.3t
			24.7t	13.8t	25.1t
			22.5t	8.8t	24.9t
			22.4t		24.8t
			21.9t		24.6t
			21.7t		23.1t
					22.5t
					21.9t
					21.3t

Coupling constants derived from proton-coupled spectra. [a] dq, $^3J_{CO,H}$ 11.3, $^3J_{CO,Me}$ 3.6 Hz. [b] dq, $^2J_{CO,H}$ 2.1, $^3J_{CO,Me}$ 3.8 Hz. [c] dq, $^3J_{CO,H}$ 6.9, $^3J_{CO,Me}$ 3.3 Hz. [d] dq, $^2J_{CO,H}$ 2.3, $^3J_{CO,Me}$ 3.9 Hz.

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

	Adduct					
	A (2a)	B (2b)	C (2c)	D (2d)	(2e)	(2f)
Ketone (CO)	183.6s [a]	183.8s [c]	184.1s [e]	183.7s [g]	183.9s [i]	184.2s [k]
Ester (CO)	166.2s [b]	166.2s [d]	166.6s [f]	166.5s [h]	166.8s [j]	167.0s [l]
sp^2-C	176.2s	175.5s	171.2s	170.4s	170.3s	171.5s
	144.9s	143.7s	143.0s	143.1s	142.8s	146.8s
	143.8s	140.8s	141.5s	141.5s	142.3s	143.1s
	133.1s	132.0s	131.7s	131.6s	130.3s	131.5s
		121.0s	121.3s	121.4s	121.1s	112.4s
			105.8s	112.8s	111.9s	
sp^2-CH	136.6d	136.8d	135.9d	135.9d	136.3d	136.1d
	128.5d	127.3d	127.3d	127.4d	127.4d	128.4d
	125.0d	123.2d	122.7d	122.5d	123.1d	125.2d
	121.8d	121.7d	121.3d	121.4d	121.8d	122.1d
	108.7d	95.8d				108.4d
	96.5d					
sp^3-C	51.8s	52.8s	53.1s	53.0s	57.5s	57.0s
OMe	52.2q	52.2q	52.2q	52.1q	52.1q	52.2q
CMe	39.1q	38.8q	39.5q	39.6q		
			10.0q	15.7q		
NCH_2/NMe	29.4q	41.3t	45.1t	44.7t	44.8t	32.7q
sp^3-CH_2		24.1t	24.2t	24.2t	50.1t	50.6t
					28.3t	28.2t
		21.2t	22.3t	22.3t	26.7t	26.7t
					25.8t	25.9t
				17.0t	24.2t	23.2t
					22.9t	22.6t
					22.4t	22.3t
					22.4t	22.1t
					22.3t	19.1t
					21.7t	
					18.9t	

[a] d, $^2J_{CO,H}$ 0.9. [b] dq, $^3J_{CO,H}$ 6.7, $^3J_{CO,CH_3}$ 3.6 Hz. [c] d, $^2J_{CO,H}$ 1.0 Hz. [d] dq, $^3J_{CO,H}$ 6.2, $^3J_{CO,CH_3}$ 3.9 Hz. [e] q, $^3J_{CO,Me}$ 3.7 Hz. [f] dq, $^3J_{CO,H}$ 6.1, $^3J_{CO,CH_3}$ 3.9 Hz. [g] dd, $^3J_{CO,CH_2}$ 4.8, 4.8 Hz. [h] dq, $^3J_{CO,H}$ 6.1, $^3J_{CO,CH_3}$ 3.8 Hz. [i] dd, $^3J_{CO,CH_2}$ 4.3, 5.0 Hz. [j] dq, $^3J_{CO,H}$ 8.1, $^3J_{CO,CH_3}$ 4.0 Hz. [k] dd, $^3J_{CO,CH_2}$ 4.6, 4.6 Hz. [l] dq, $^3J_{CO,H}$ 6.9, $^3J_{CO,CH_3}$ 4.2 Hz.

Table 3. I.r., u.v., and ^1H n.m.r. data of (1 + 1 DMAD–CH_4O) adducts

	Adduct					
	(2a)	(2b)	(2c)	(2d)	(2e)	(2f)
Symbol	A	B	C	D		
I.r., CO freq. (cm^{-1})	1 720 [7]	1 715	1 713	1 715	1 712	1 721
	1 640	1 640	1 626	1 632	1 625	1 631
U.v. [nm(log ε)]	238 (4.4) [7]	236 (4.17)	244 (4.30)	244 (4.24)	248 (4.25)	240 (4.20)
	278 (4.0)	274 (3.81)	278 (4.22)	278 (3.94)	280 (4.0)	283 (3.87)
	324 (3.6)					
	422 (3.8)	415 (3.66)	437 (3.89)	435 (3.84)	440 (3.89)	430 (3.68)
^1H N.m.r.	6.89 [a,7]	6.88 [b]	6.86s	6.84s	6.80s	6.83s
δ(Olefin H)	5.67 [a]	5.59 [b]				

[a] d, *J* 1.5 Hz. [b] d, *J* 1.0 Hz.

Reaction of the Indole (1a) *with Dimethyl Acetylenedicarboxylate* (*DMAD*).—The indole (1a) (2.0 g) and DMAD (3.0 g) were refluxed in acetic acid (25 ml) for 3 days, by which time all the indole had been consumed (t.l.c.). Evaporation under reduced pressure gave a tarry residue which was purified by column chromatography on alumina with toluene, and from which three crystalline products were obtained. (i) The most polar compound *dimethyl* 1,3-*dimethylindol*-2-*ylmaleate* (1c) was obtained as yellow plates (0.25 g) (from ether), m.p. 81—82 °C (Found: C, 66.8; H, 6.0; N, 5.0. $C_{16}H_{17}NO_4$ requires C, 66.9; H, 5.9; N, 4.9%); $\lambda_{max.}$ 226 (ε 22 000), 260 (8 000), 277 (6 000), and 340 nm (9 500); *m*/*z* 287 (M^+, 92%), 228 (35), 227 (26), 170 (20), 169 (41), and 168 (100); δ 7.6—7.4 (1 H, m), 7.3—7.0 (3 H, m), 6.11 (1 H, s, olefinic H), 3.84 (3 H, s), 3.81 (3 H, s), 3.65 (3 H, s), and 2.33 (3 H, s). (ii) *Dimethyl* 1,3-*dimethylindol*-2-*ylfumarate* (1d) was obtained as crimson rhombs (0.5 g) (from ether), m.p. 103—104 °C (Found: C, 67.1; H, 6.0; N, 5.0. $C_{16}H_{17}NO_4$ requires C, 66.9; H, 5.9; N, 4.9%); $\lambda_{max.}$ 225 (ε 22 000) and 295 nm (9 500); *m*/*z* 287 (M^+, 100%), 228 (33), 227 (27), 169 (37), and 168 (97); δ 7.6—7.4 (1 H, m), 7.29 (1 H, s, olefinic H), 7.28—6.9 (3 H, m), 3.68 (3 H, s), 3.50 (3 H, s), 3.48 (3 H, s), and 2.12 (3 H, s). (iii) The least polar compound, (E)-*methyl* 1,3-*dimethylindol*-2-*ylacrylate* (1e) was obtained as yellow needles (0.1 g) (from ether), m.p. 108—110 °C (Found: C, 73.2; H, 6.6; N, 6.2. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%);

$\lambda_{max.}$ 223 (ε 14 000), 259 (4 000), and 347 nm (6 500); *m/z* 229 (M^+, 100%), 214 (33), 198 (19), 170 (66), 169 (44), and 168 (39); δ 7.86 (1 H, d, *J* 19 Hz), 7.65—7.45 (1 H, m), 7.3—6.9 (3 H, m), 6.24 (1 H, d, *J* 19 Hz), 3.77 (3 H, s) and 3.73 (3 H, s), and 2.44 (3 H, s).

Reaction of the Indole (1a) *with Methyl Propiolate.*—The indole (1a) (1 g) and methyl propiolate (0.7 g) were refluxed in 90% acetic acid (25 ml) for 2 days. Evaporation and column chromatography (toluene) gave the acrylate (1e) (0.5 g).

Reaction of the Indole (1b) *and Dimethyl Acetylenedicarboxylate.*—The indole (1b) (2.0 g) and DMAD (3.2 g) were refluxed in 90% acetic acid (25 ml) for 3 days. Evaporation gave a brown residue which was chromatographed by h.p.l.c. with toluene, and then chloroform. The chloroform fraction was rechromatographed on alumina (chloroform) giving yellow plates (0.8 g) (from ether) of *methyl* 4a,9-*dimethyl*-2-*oxo*-2,4a-*dihydrocarbazole*-4-*carboxylate* (2a), m.p. 143—145 °C (Found: C, 71.2; H, 5.6; N, 5.2. Calc. for $C_{16}H_{15}NO_3$: C, 71.4; H, 5.6; N, 5.2%); *m/z* 269 (M^+, 70%), 254 (100), 226 (66), and 182 (32); δ 8.0—7.8 (1 H, m), 7.4—6.8 (3 H, m), 6.75 (1 H, d, *J* 1.5 Hz), 5.60 (1 H, d, *J* 1.5 Hz), 3.83 (3 H, s), 3.20 (3 H, s), and 1.80 (3 H, s).

Reaction of the Indole (3c) *and Dimethyl Acetylenedicarboxylate.*—The indole (3c) (1 g) and DMAD (2 g) in 98% acetic acid (25 ml) were kept at 100 °C for 1½ days and then evaporated. T.l.c. (chloroform) gave numerous coloured bands; crystalline material was obtained from only one of these (R_F 0.45) as orange prisms (0.25 g) (from benzene–light petroleum) of *methyl* 11a-*methyl*-9-*oxo*-5,6,9,11a-*tetrahydro*-4H-*pyrido*[3,2,1-jk]*carbazole*-11-*carboxylate* (2b), m.p. 154—155 °C (Found: C, 73.0; H, 5.9; N, 4.7. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.7%); *m/z* 295 (M^+, 90%), 281 (90), and 253 (100); δ 7.7 (1 H, m), 7.1—6.75 (2 H, m), 6.88 (1 H, d, *J* 1.5 Hz), 5.59 (1 H, d, *J* 1.5 Hz), 3.90 (3 H, s), 3.85—3.3 (2 H, m), 2.9—2.7 (2 H, m), 2.3—2.0 (2 H, m), and 1.87 (3 H, s).

Reaction of the Indole (3d) *and Dimethyl Acetylenedicarboxylate.*—The indole (0.7 g) (3d) and DMAD (1.2 g) in 98% acetic acid (75 ml) was kept at 100 °C for 3 days and then evaporated. T.l.c. (chloroform) gave several bands which yielded gums, and from the red-orange band (R_F 0.45), red prisms (0.2 g) (from ethanol) were obtained of *methyl* 8,11a-*dimethyl*-9-*oxo*-5,6,9,11a-*tetrahydro*-4H-*pyrido*[3,2,1-jk]-*carbazole*-11-*carboxylate* (2c), m.p. 174—175 °C (Found: C, 73.6; H, 6.2; N, 4.3. $C_{19}H_{19}NO_3$ requires C, 73.7; H, 6.2; N, 4.5%); *m/z* 309 (M^+, 71%) and 295 (100); δ 7.65 (1 H, d, *J* 7.4 Hz), 7.1—6.7 (2 H, m), 6.86 (1 H, s, olefinic H), 4.6—3.8 (2 H, m), 3.88 (3 H, s), 2.9—1.8 (4 H, m), 2.23 (3 H, s), and 1.84 (3 H, s).

Reaction of the Indole (3e) *and Dimethyl Acetylenedicarboxylate.*—The indole (0.7 g) (3e) and DMAD (1.2 g) in 95% acetic acid (50 ml) were kept at 100 °C for 2 days and then evaporated. T.l.c. (chloroform) was carried out; the product from the red band (R_F 0.45) giving, after trituration with light petroleum (b.p. 40—60 °C), orange prisms (0.15 g) (from ethanol) of *methyl* 8-*ethyl*-11a-*methyl*-9-*oxo*-5,6,9,11a-*tetrahydro*-4H-*pyrido*[3,2,1-jk]*carbazole*-11-*carboxylate* (2d), m.p. 148—149 °C (Found: C, 74.35; H, 6.7; N, 4.5. $C_{20}H_{21}NO_3$ requires C, 74.3; H, 6.55; N, 4.3%); *m/z* 323 (M^+, 90%), 308 (100), 295 (40), and 265 (50); δ 7.6 (1 H, d, *J* 7 Hz), 7.1—6.7 (2 H, m), 6.84 (1 H, s, olefinic H), 4.4—3.6 (2 H, m), 3.87 (3 H, s), 2.9—2.0 (6 H, m), 1.84 (3 H, s), and 1.12 (3 H, t, *J* 7.4 Hz).

Reaction of the Indole (3f) *and Dimethyl Acetylenedicarboxylate.*—The indole (3f) (1 g) and DMAD (2 g) in 98% aqueous acetic acid (50 ml) were heated at 100 °C for 3 days and then evaporated and t.l.c. (chloroform) carried out. Only one band (R_F 0.5) gave a crystalline product as orange prisms (0.2 g) (from ethanol) of *methyl* 9-*oxo*-5,6,9,11-*tetrahydro*-4H-8,11a-*nonanopyrido*[3,2,1-jk]*carbazole*-11-*carboxylate* (2e), m.p. 167.5—168 °C (Found: C, 76.85; H, 7.7; N, 3.4. $C_{26}H_{31}NO_3$ requires C, 77.0; H, 7.7; N, 3.45%); *m/z* 405 (M^+, 100%) and 346 (30); δ 7.75—7.6 (1 H, m), 7.1—6.8 (2 H, m), 6.80 (1 H, s, olefinic H), 4.5—1.0 (24 H, m), and 3.85 (3H, s).

Reaction of the Indole (3b) *and Dimethyl Acetylenedicarboxylate.*—The indole (3b) (0.8 g) and DMAD (1.5 g) in 98% acetic acid were heated at 100 °C for 3 days and then evaporated and t.l.c. (chloroform) carried out. From the orange coloured band (R_F 0.5), orange prisms (0.18 g) (diethyl ether) were obtained of *methyl* 9-*methyl*-7-*oxo*-4b,7-*dihydro*-4b,8-*nonanocarbazole*-5-*carboxylate* (2f), m.p. 155—156 °C (Found: C, 75.95; H, 7.9; N, 3.65. $C_{24}H_{29}NO_3$ requires C, 75.95; H, 7.7; N, 3.7%); *m/z* 379 (M^+, 94%), 268 (100), 255 (59), and 320 (11); δ 7.90—6.90 (4 H, m), 6.83 (1 H, s, olefinic H), 3.87 (3 H, s), 3.56 (3 H, s), and 2.7—0.4 (18 H, m).

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