Oxazolo[3,2-*a*]indoles, Pyrrolo- and Azepino-[1,2-*a*]indoles from 3*H*-Indole 1-Oxides and Acetylenecarboxylic Esters by Skeletal Rearrangements

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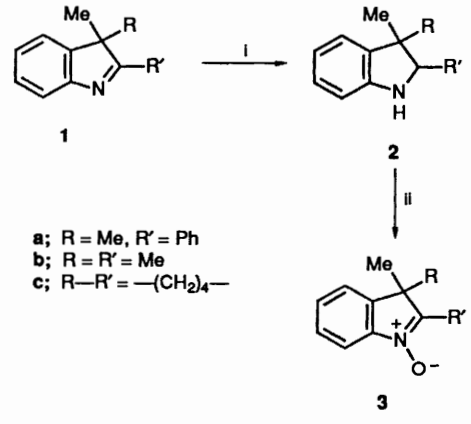
3*H*-Indole *N*-oxides **3** have been prepared from 3*H*-indoles **1** by hydride reduction followed by *m*-chloroperbenzoic acid oxidation. Reaction of **3** with dimethyl acetylenedicarboxylate (DMAD) and with methyl propiolate (MP), give a variety of products, all apparently formed by rearrangement of the initial isoxazole 1,3-dipolar cycloadduct, with the type of reaction being dependent on the 2-substituent in **3**: the 2-phenyl derivative of **3** gives oxazolo[3,2-*a*]indoles **5**, and when **3** posseses a methyl or methylene substituent at C-2, both DMAD and MP give pyrrolo[1,2-*a*]indoles **6**, with the MP reactions also yielding an azepino[1,2-*a*]indole **7** in each case. The structures of the products have been established by spectroscopy with those of **5b** and **7b** being confirmed by X-ray crystallography.

Apart from the isatogens,[1] few 3*H*-indole 1-oxides have been reported. Sterically hindered 3,3-disubstituted 3*H*-indole 1-oxides have been prepared by Döpp[2,3] by photolysing *o*-nitro-*tert*-butylbenzenes, and Mousseron-Canet and Boca[4] have prepared 2,3,3-trimethyl-3*H*-indole 1-oxide and others by reduction and cyclisation of *o*-nitro-alkylketobenzenes. All these routes to 3*H*-indole 1-oxides rely on the synthesis of complex *o*-nitrobenzene derivatives. Unfortunately, perbenzoic acid oxidation of 3*H*-indoles has not been found to lead to the corresponding 1-oxides.[5]

Apart from the reactions of isatogens, no reports of the addition of acetylenes to 2,3,3-trisubstituted 3*H*-indole 1-oxides have appeared. Isatogens have been reported[1] to react with DMAD to give isoxazolines,[1] and in some cases these reacted further to give quinolones.[1,6] Nitrones have also been reported to react with DMAD to give isoxazolines[7] which are generally thermally unstable and in some cases have been found to rearrange to pyrroles[8–11] or oxazolines[7] when heated.

We now report that the method of hydride reduction followed by *m*-chloroperbenzoic acid oxidation used for the preparation of isatogens from indolines,[12] is a satisfactory route for the preparation of a variety of 2,3,3-trisubstituted 3*H*-indole 1-oxides; in particular, we have prepared the *N*-oxides **3a–c** (see Scheme 1) as stable oils from the readily available 3*H*-indoles



Scheme 1 *Reagents:* i, $NaBH_4$; ii, *m*-$ClC_6H_4CO_3H$

1a–c. The *N*-oxides all exhibit characteristic M − 17 peaks in their mass spectra, and in their ^{13}C NMR spectra the imine carbon resonances (C-2 of the indole or C-9a in the carbazole) shift upfield from δ *ca.* 185 in **1** to δ 140–150 in **3**.

Results and Discussion

Treatment of 3,3-dimethyl-2-phenyl-3*H*-indole 1-oxide **3a** with DMAD or MP gives reasonable yields of a stable crystalline 1:1 adduct in each case. From known analogous reactions, *e.g.* isatogens and DMAD,[1] very likely structures for these adducts are the isoxazolo[2,3-*a*]indoles **4a** and **4b** respectively formed by 1,3-dipolar cycloaddition; their ^{13}C NMR spectra, whilst exhibiting the necessary two quaternary sp^3 carbon signals, do however reveal that an isoxazole structure is unlikely as one of the quaternary sp^3 carbon signals in each compound (at δ_C 101.9 and 109.0 respectively), resonates at a much lower field than expected: an sp^3 carbon attached to N and C usually resonates in the region δ 78–84.[13] The signals at δ 101.9 and 109.0 are in fact characteristic of an sp^3 carbon attached to two hetero-atoms,[13] thus indicating the oxazolo[3,2-*a*]indole structures **5a** and **5b** (or **5c**) for the DMAD and MP adducts respectively. These structures are supported by their spectra (see Table 1 for ^{13}C NMR data). We are unable to distinguish between structures **5b** and **5c** on spectroscopic grounds; both structures would be expected to exhibit a lowfield ^1H and ^{13}C NMR signal for the olefinic hydrogen (*e.g.* H-2 in **5b**). The observed signal is found at δ_H 10.0(s) and δ_C 184.9(d). The actual structure has been determined using X-ray diffraction which showed the structure to be **5b** (see Fig. 1). The formation

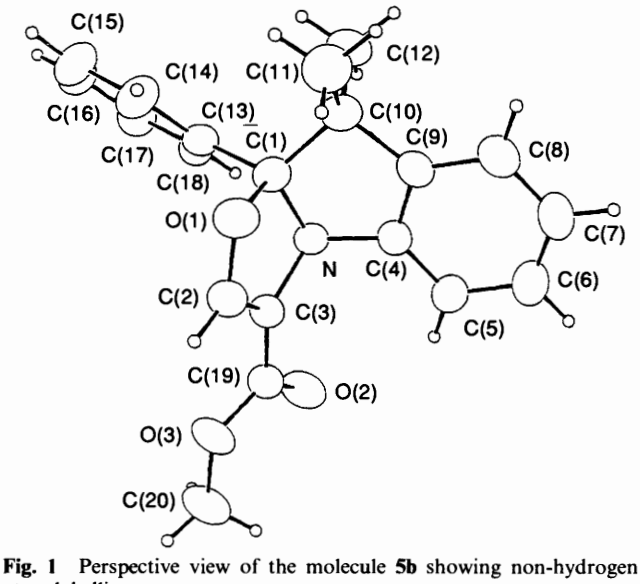


Fig. 1 Perspective view of the molecule **5b** showing non-hydrogen atom labelling

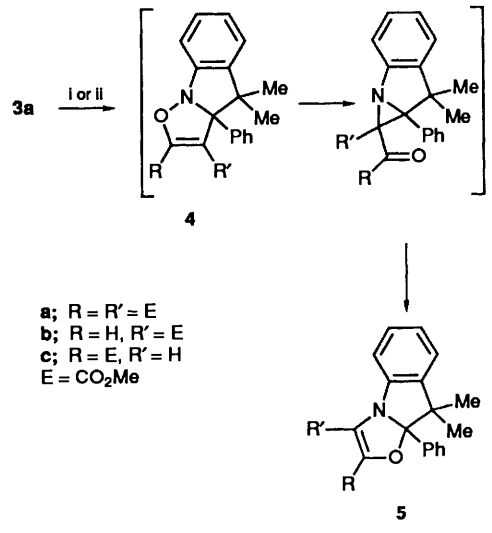
Table 1 ^{13}C NMR spectra of adducts recorded as δ values (from internal tetramethylsilane). The multiplicities observed on off-resonance decoupling are noted

Assignments	Compounds									
	5a	**5b**	**6a**	**6b**	**6c**	**6d**	**6e**	**6f**	**7a**	**7b**
Ester CO(s)	181.9	171.7	164.9	165.4	161.3	165.5	161.8	165.7	181.9	168.6
	178.5		162.0	161.3					165.9	166.1
sp^2–C(s)	167.2	166.6	149.4	152.1	153.6	146.7	155.7	148.4	163.7	163.5
	164.6	144.3	145.5	148.1	145.2	145.6	148.0	148.0	144.4	144.4
	143.0	139.3	138.7	140.6	139.9	138.3	141.5	140.3	137.7	138.5
	141.0	136.6	127.9	128.0	118.0	120.3	116.3	119.9	130.9	132.9
	138.4		124.3	124.5			116.3	117.3	126.2	127.7
				117.8						114.6
sp^2–CH(d)	129.7	184.9	127.9	128.0	127.8	127.7	127.9	127.7	147.7	149.0
	129.7	129.7	125.6	125.0	124.4	124.9	123.9	124.3	132.4	129.0
	128.4	129.7	123.0	122.8	123.2	123.5	123.5	124.0	127.4	127.2
	127.6	129.1	114.6	114.9	122.5	114.4	122.9	122.4	122.3	121.6
	126.6	128.2	102.4		115.6	110.6	115.2	111.6	121.7	121.6
	126.6	128.2			100.6	101.0			109.1	108.9
	124.7	128.0							101.1	
	122.0	123.9								
	110.5	121.8								
		110.1								
sp^3–C(s)	101.9	109.0	40.9	40.0	40.8	41.5	40.1	40.2	47.6	47.0
	51.3	49.1								
sp^3–CH_2(t)				32.3			32.5	32.8		30.2
				21.2			21.2	22.5		27.2
				20.1			19.9	20.6		18.0
CMe(q)	25.0	29.0	27.5	25.2	27.6	27.9	25.2	25.6	27.9	26.1
	25.0	29.0	27.5		27.6	27.9			27.9	
OMe(q)	51.2	51.4	52.3	52.0	51.2	51.4	51.3	50.9	52.1	52.1
	52.3		51.8	51.6					52.0	52.1

Table 2 ^1H NMR assignments of the pyrrole ring ^1Hs in **6**; δ_H in ppm and J in Hz

Compound	1-H	2-H	3-H
6a	6.46	—	—
6c	6.08 (d, J 3.7)	7.14 (d, J 3.7)	—
6d	6.48 (d, J 1.1)	—	7.64 (d, J 1.1)
6e	—	6.92	—
6f	—	—	7.62

of **5a** and **5b** may be rationalised by invoking a rearrangement of the initially formed isoxazolo[2,3-*a*]indole **4a** or **4b** as shown in Scheme 2. This rearrangement of 4-isoxazoles to 4-oxazoles



Scheme 2 *Reagents:* i, DMAD; ii, MP

has been reported[7] and an aziridine intermediate has been isolated from such reactions.[7] It has also been reported[10] that MP adds to nitrones to give the 4-methoxycarbonylisoxazoles; the isolation of **5b** and the mechanism in Scheme 2, indicate that the addition of MP to the indole 1-oxide **3a** follows with similar regiospecificity forming a 4-methoxycarbonylisoxazole intermediate **4b**.

The reactions of the 3*H*-indole *N*-oxides **3b** and **3c** with DMAD and MP give very different products from that of **3a**. With DMAD, both give good yields of adducts with the stoichiometric formula (1 *N*-oxide + 1 DMAD − H_2O); in each case NMR spectra (see Table 1) reveal two methyl ester groups and show that an aliphatic carbon in **3** has reacted by losing two hydrogen atoms. This data indicates the pyrroloindole structures **6a** and **6b**; for the products from **3b** and **3c** respectively, and is supported by their UV absorbance which is reminiscent of that reported for 9*H*-pyrrolo[1,2-*a*]indoles.[14] With MP both *N*-oxides **3b** and **3c**, give three products, two of which in each case, exhibit UV, NMR and mass spectra reminiscent of **6a** and **6b**; consequently, the products from *N*-oxide **3b** have been assigned structures **6c–d**, with the position of the ester substituents following from the coupling constants of their higher field aromatic or pyrrole ring protons (see Table 2), and the products from **3c** have been assigned the pyrrolo[3,2,1-*jk*]carbazole structures **6e–f** from a comparison of their ^1H NMR spectral data with that of **6c–d** (see Table 2). The third product from the MP reactions was a black crystalline (1 *N*-oxide + 2 MP − H_2O) adduct in each case, with each exhibiting spectra consistent with an azepino[1,2-*a*]indole structure and supported by their ^{13}C NMR spectra (see Table 1) which both show 14 sp^2 carbons. *A priori*, 4 different substituted azepino[1,2-*a*]indole structures are possible for each of these two adducts, *viz.* those with ester groups at 2 : 3, 2 : 5, 3 : 4 and 3 : 5 of the azepine ring. Unfortunately, the ^1H NMR coupling constants of the azepine ring protons could not be used to distinguish between the structures, as the signals were

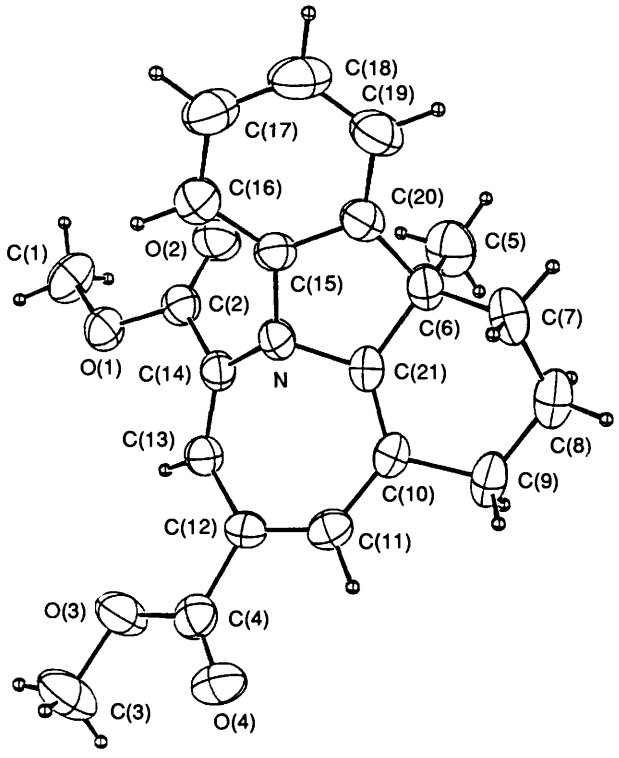
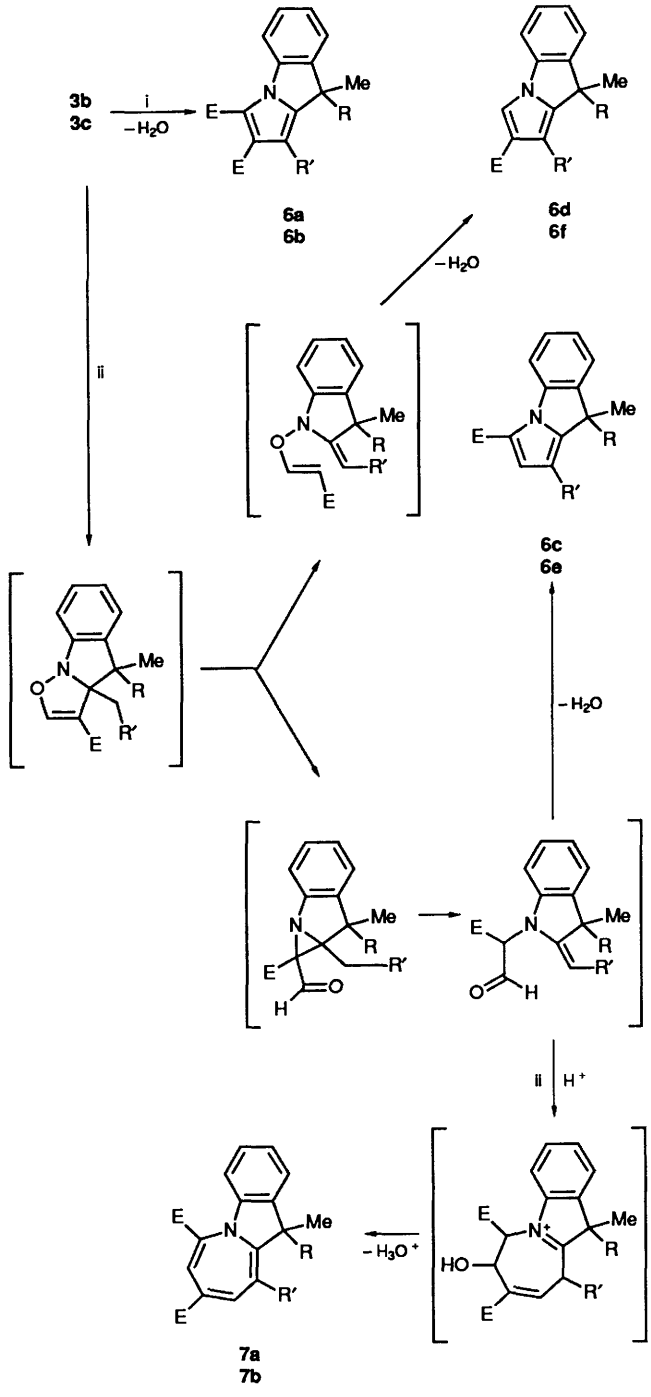


Fig. 2 Perspective view of the molecule **7b** showing non-hydrogen atom labelling

overlapped by the benzenoid protons. In order to solve this problem a single crystal X-ray structure determination was carried out on the adduct from **3c** and was found to have the structure **7b** (see Fig. 2). From a comparison of their spectral data the adduct from **3b** is assigned structure **7a**. Pyrrolo- or azepino-, -indoles (or -carbazoles) have not previously been reported from reactions of 3*H*-indole 1-oxides with acetylenes. Two mechanisms for the formation of pyrroles from nitrones and acetylenes have been proposed, one involving a Hetero–Cope rearrangement[8] and the other, *via* an aziridine intermediate.[7] These mechanisms may be used to account for the formation of the pyrrolo-adducts **6a–f** as shown in Scheme 3. The formation of both regioisomers from the MP reactions suggests that either both mechanisms are operating or less likely, that two different isoxazoles are formed and that these then rearrange *via* one of the mechanisms. The formation of the azepino derivatives may also be accounted for by using an intermediate from the aziridine route, which in this case takes part in a Michael addition with another molecule of MP as shown in Scheme 3.

It is interesting to note that all the reaction products from the 3*H*-indole 1-oxide reactions reported in this paper appear to have been formed *via* skeletal rearrangements, thus indicating further examples of isoxazolines (*e.g.* **4a** and **4b**) which are thermally unstable;[7] and, furthermore, none of the products are analogous to those obtained from isatogens and acetylenecarboxylic esters. These reactions also show that like many 1*H*- and 3*H*-indole[15] reactions with acetylenes, the substituent at C-2 plays an important role in product formation: in particular, when a hydrogen is present on the carbon atom attached to C-2, further reactions occur involving that carbon atom.

These reactions provide routes to several ring systems of current interest, and considering the ready availability of the 3*H*-indole starting materials, these reactions have considerable potential for the synthesis of further analogues and derivatives. The 9*H*-pyrrolo[1,2-*a*]indole skeleton, first reported in 1955,



a, c, d; R = Me, R′ = H
b, e, f; R—R′ = —$(CH_2)_3$—
E = CO_2Me

Scheme 3 *Reagents:* i, DMAD; ii, MP

has been synthesised by several routes, no doubt prompted by their anticancer and hypoglycaemic properties.[16] Hexahydropyrrolo[3,2,1-*jk*]carbazoles have been synthesised from tetrahydrocarbazoles possessing a 1-acetic ester side chain.[17] Azepino[1,2-*a*]indoles have been synthesised by Jones[18] *via* intramolecular nitrene insertions involving thermal decomposition of phenyl azides. No routes appear to be known for azepino[3,2,1-*a*]carbazoles with structures analogous to **7b**.

Experimental

General Details.—^1H and ^{13}C NMR spectra were determined

at 89.56 and 22.50 MHz respectively on a JEOL FX90Q Fourier Transform spectrometer for $CDCl_3$ solutions with tetramethylsilane as an internal standard; J values are given in Hz, and the multiplicities in ^{13}C spectra were obtained by off-resonance decoupling. IR spectra were determined as Nujol mulls. Mass spectra were recorded on an Hitachi RMS-4, and accurate mass determinations were measured on a VGMM 70-70 mass spectrometer.

Synthesis of 3H-*Indole* N-*Oxides: General Procedure.*—The 3*H*-indoles **1**, prepared by treating phenylhydrazones with boiling acetic acid, were first converted into indolines **2** by reaction with equimolar portions of sodium borohydride in methanol,[19] and purified by column chromatography. To the indoline **2** (15 mmol) dissolved in dichloromethane (30 cm^3) at 0 °C, 3-chloroperbenzoic acid (40 mmol) was slowly added. After further cooling for 20 min the mixture was filtered off and the filtrate evaporated before purification using silica gel column chromatography [light petroleum (b.p. 40–60 °C)–ether, 1:1]; the column was finally eluted with ethyl acetate (500 cm^3) which on evaporation yielded the 3*H*-indole *N*-oxide **3**.

The phenylhydrazone of isobutyrophenone gave a pale yellow oil of 3,3-dimethyl-2-phenyl-3*H*-indole **1a**, b.p. 140 °C/2.5 mmHg (lit.,[20] b.p. 152–156 °C/4 mmHg); *m/z* 221 (M^+, 100%) and 206 (35); δ_H 8.2–7.8 (2 H, m, ArH), 7.51–7.50 (1 H, m, ArH), 7.4–7.2 (6 H, m, ArH) and 1.49 (6 H, s, 2 × Me). Reduction of **1a** gave colourless prisms of 3,3-dimethyl-2-phenylindoline **2a**, m.p. 92–93 °C (lit.,[21] m.p. 93 °C); *m/z* 223 (M^+, 100%) 208 (89) and 193 (17); δ_H 7.5–7.2 (5 H, m, ArH), 7.1–7.0 (2 H, m, ArH), 6.8–6.7 (2 H, m, ArH), 4.58 (1 H, s, CH), 4.0 (1 H, br s, NH), 1.42 (3 H, s, Me) and 0.72 (3 H, s, Me). Oxidation gave a pale brown oil of 3,3-*dimethyl*-2-*phenyl*-3H-*indole* 1-*oxide* **3a** (35%) (Found: M^+, 237.1159. $C_{16}H_{15}NO$ requires *M*, 237.1149); λ_{max}/nm (ε) 239 (8200), 318 (13 100), 330 (13 900) and 346 (8700); *m/z* 237 (M^+, 100%), 222 (46) and 220 (28); δ_H 8.6–8.5 (2 H, m, ArH), 7.9–7.7 (1 H, m, ArH), 7.6–7.4 (6 H, m, ArH) and 1.67 (6 H, s, 2 × Me).

The phenylhydrazone of 3-methylbutan-2-one gave a pale yellow oil of 2,3,3-trimethyl-3*H*-indole **1b**, b.p. 76 °C/1.5 mmHg (lit.,[22] b.p. 113 °C/21 mmHg); *m/z* 159 (M^+, 66%) and 144 (100); δ_H 6.95–7.52 (4 H, m, ArH), 2.13 (3 H, s, Me) and 1.18 (6 H, s, 2 × Me). Reduction of **1b** gave a pale yellow oil of 2,3,3-trimethylindoline **2b**,[23] *m/z* 161 (M^+, 59%) and 146 (100); δ_H 6.5–7.1 (4 H, m, ArH), 3.6 (1 H, br s, NH), 3.44 (1 H, q, *J* 6.6, 2-H), 1.25 (3 H, s, Me), 1.11 (3 H, d, *J* 6.6, Me) and 1.01 (3 H, s, Me). Oxidation yielded 2,3,3-trimethyl-3*H*-indole 1-oxide **3b** (33%) as an oil (Found: M^+, 175.0999. $C_{11}H_{13}NO$ requires *M*, 175.0997); λ_{max}/nm (ε) 232 (12 400), 316 (13 300), 330 (13 300) and 345 (8200); *m/z* 175 (M^+, 100%), 160 (98) and 158 (19); δ_H 7.8–7.7 (1 H, m, ArH), 7.5–7.4 (3 H, m, ArH), 2.30 (3 H, s, Me) and 1.39 (6 H, s, 2 × Me) [lit.,[4] reports δ_H 7.31 (4 H, ArH), 2.19 (3 H, Me) and 1.39 (6 H, 2 × Me)].

The phenylhydrazone of 2-methylcyclohexanone gave a pale yellow oil of 4a-methyl-4a*H*-1,2,3,4-tetrahydrocarbazole **1c**, b.p. 90–100 °C/5.8 mmHg (lit.,[24] b.p. 143 °C/10 mmHg); *m/z* 185 (M^+, 53%), 184 (40) and 170 (100); δ_H 7.55–6.88 (4 H, m, ArH), 3.0–0.8 (8 H, m, 4 × CH_2) and 1.23 (3 H, s, Me). Reduction of **1c** gave a pale yellow oil of indoline **2c**,[25] *m/z* 187 (M^+, 68%), 172 (56) and 144 (100); δ_H 7.1–6.5 (4 H, m, ArH), 3.5 (1 H, br s, NH), 3.3 (1 H, m, CH), 1.70–0.9 (8 H, s, 4 × CH_2) and 1.25 (3 H, s, Me). Oxidation gave a brown oil of 1,2,3,4-*tetrahydro*-4a-*methyl*-4a*H*-*carbazole* 9-*oxide* **3c** (34%) (Found: M^+, 201.1187. $C_{13}H_{15}NO$ requires *M*, 201.1149); λ_{max}/nm (ε) 239 (7900), 318 (12 400), 331 (13 100) and 346 (8400); *m/z* 201 (M^+, 100%), 186 (22), 184 (22) and 159 (20); δ_H 7.9–7.6 (1 H, m, ArH), 7.5–7.4 (3 H, m, ArH), 3.6–3.4 (1 H, m, CH), 2.3–1.0 (7 H, m, 3 × CH_2 and CH) and 1.39 (3 H, s, Me).

Reactions of 3H-*Indole* N-*Oxides with Dimethyl Acetylenedicarboxylate: General Procedure.*—The *N*-oxide (2.5 mmol) and DMAD (7.5 mmol) were heated under reflux in toluene (15 cm^3) until all the *N*-oxide had been consumed as indicated by TLC. The solvent was evaporated and the residue purified by TLC [light petroleum (b.p. 60–80 °C)–diethyl ether 1:1].

After being heated for 18 h, **3a** gave yellow prisms (R_f 0.70) of *dimethyl* 9,9a-*dihydro*-9,9-*dimethyl*-9a-*phenyloxazolo*[3,2-a]-*indole*-2,3-*dicarboxylate* **5a** (0.52 g, 55%), m.p. 116–118 °C (from chloroform–hexane) (Found: C, 69.2; H, 5.65; N, 3.7. $C_{22}H_{21}NO_5$ requires C, 69.6; H, 5.6; N, 3.7%); ν_{max}/cm^{-1} 1720s and 1710s; λ_{max}/nm (ε) 254 (10 800), 290 (3800) and 395 (12 500); *m/z* 379 (M^+, 6.5%) and 320 (100); δ_H 7.56–6.96 (8 H, m, ArH), 6.52–6.38 (1 H, m, ArH), 3.73 (3 H, s, OMe), 3.12 (3 H, s, OMe) and 1.83 (6 H, s, 2 × CMe).

After being heated for 2 h, **3b** gave a pale yellow oil (R_f 0.70) of *dimethyl* 9,9-*dimethyl*-9H-*pyrrolo*[1,2-a]*indole*-2,3-*dicarboxylate* **6a** (0.37 g, 50%) (Found: M^+, 299.1154. $C_{17}H_{17}NO_4$ requires *M*, 299.1157); ν_{max}/cm^{-1} 1722s and 1702s; λ_{max}/nm (ε) 224 (3100) and 292 (18 600); *m/z* 299 (M^+, 49%), 284 (100), 268 (17) and 240 (30); δ_H 8.04–7.98 (1 H, m, ArH), 7.44–7.18 (3 H, m, ArH), 6.46 (1 H, s, olefinic H), 3.98 (3 H, s, OMe), 3.86 (3 H, s, OMe) and 1.49 (6 H, s, 2 × CMe).

After being heated for 24 h **3c** gave pale yellow needles (R_f 0.75) of *dimethyl* 1,2,3,10b-*tetrahydro*-10b-*methylpyrrolo*[3,2,1-*jk*]*carbazole*-4,5-*dicarboxylate* **6b** (0.39 g, 48%), m.p. 105–106 °C (from hexane) (Found: M^+, 325.1329. $C_{19}H_{19}NO_4$ requires *M*, 325.1313); ν_{max}/cm^{-1} 1720s and 1696s; λ_{max}/nm (ε) 296 (15 400); *m/z* 325 (M^+, 49%), 284 (100), 268 (17) and 240 (30); δ_H 7.94–7.76 (1 H, m, ArH), 7.32–6.92 (3 H, m, ArH), 3.94 (3 H, s, OMe), 3.85 (3 H, s, OMe); 2.84–0.96 (6 H, m, 3 × CH_2) and 1.45 (3 H, s, CMe).

Reactions of 3H-*Indole* N-*Oxides with Methyl Propiolate: General Procedure.*—A mixture of the *N*-oxide (5 mmol) and MP (15 mmol) was heated under reflux in toluene (15 cm^3) until all the *N*-oxide had been consumed as indicated by TLC. The solvent was evaporated and the residue separated into components by TLC [light petroleum (60–80 °C)–diethyl ether 3:1].

After being heated for 30 h, **3a** gave pale yellow prisms (R_f 0.35) of methyl 9,9a-*dihydro*-9,9-*dimethyl*-9a-*phenyloxazolo*-[3,2-a]*indole*-3-*carboxylate* **5b** (0.32 g, 20%), m.p. 149–150 °C (chloroform–hexane) (Found: C, 74.95; H, 5.95; H, 4.45. $C_{20}H_{19}NO_3$ requires C, 74.75; H, 5.95; N, 4.35%); ν_{max}/cm^{-1} 1725s; λ_{max}(nm (ε) 257 (19 000), 301 (8800) and 400 (900); *m/z* 321 (M^+, 27%) and 262 (100); δ_H 10.00 (1 H, s, olefinic H), 7.6–7.0 (8 H, m, ArH), 6.5–6.4 (1 H, m, ArH), 3.11 (3 H, s, OMe) and 1.83 (6 H, s, 2 × CMe).

After being heated for 2 days, **3b** separated into coloured bands from which the following were obtained. (i) The least polar pale yellow band (R_f 0.65) gave a pale yellow oil of *methyl* 9,9-*dimethyl*-9H-*pyrrolo*[1,2-a]*indole*-3-*carboxylate* **6c** (0.13 g, 10%) (Found: M^+, 241.1112. $C_{15}H_{15}NO_2$ requires *M*, 241.1098); ν_{max}/cm^{-1} 1715s; λ_{max}/nm (ε) 273 (18 700) and 285 (18 900); *m/z* 241 (M^+, 40%), 226 (100) and 182 (17); δ_H 8.60–8.46 (1 H, m, ArH), 7.38–7.10 (3 H, m, ArH), 7.14 (1 H, d, *J* 3.7, olefinic H), 6.08 (1 H, d, *J* 3.7, olefinic H), 3.87 (3 H, s, OMe) and 1.49 (6 H, s, 2 × CMe). (ii) The pale yellow band (R_f 0.45) gave colourless needles of *methyl* 9,9-*dimethyl*-9H-*pyrrolo*[1,2-a]*indole*-2-*carboxylate* **6d** (0.30 g, 25%), m.p. 74–75 °C (chloroform–hexane) (Found: M^+, 241.1079. $C_{15}H_{15}NO_2$ requires *M*, 241.1098); ν_{max}/cm^{-1} 1718s; λ_{max}/nm (ε) 234 (7200), 271 (14 900), 284 (13 500) and 293 (13 900); *m/z* 241 (M^+, 27%), 226 (100) and 182 (14); δ_H 7.64 (1 H, d, *J* 1.1, olefinic H), 7.42–7.16 (4 H, m, ArH), 6.48 (1 H, d, *J* 1.1, olefinic H), 3.84 (3 H, s, OMe) and 1.52 (6 H, s, 2 × CMe). (iii) The violet band (R_f 0.20) gave black needles of *dimethyl* 11,11-*dimethyl*-11H-*azepino*[1,2-a]-

indole-6,8-*dicarboxylate* **7a** (0.05 g, 3.0%), m.p. 102–103 °C (from chloroform–methanol) (Found: M^+, 325.1318. $C_{19}H_{19}NO_4$ requires *M*, 325.1308); ν_{max}/cm^{-1} 1720s, 1710s and 1655m; λ_{max}/nm (ε) 251 (15 000), 296 (11 100), 318 (9800) and 522 (1260); *m*/*z* 325 (M^+, 61%), 310 (100) and 266 (47); δ_H 7.13–6.53 (6 H, m, 4 ArH + 2 × olefinic H), 5.04 (1 H, d, *J* 7.57, H-1), 3.76 (3 H, s, OMe), 3.63 (3 H, s, OMe) and 1.36 (6 H, s, 2 × CMe).

After being heated for 2.5 days, **3c** separated into coloured bands from which the following were obtained. (i) The least polar pale yellow band (R_f 0.60) gave a pale yellow oil of *methyl* 1,2,3,10b-*tetrahydro*-10b-*methylpyrrolo*[3,2,1-jk]*carbazole*-5-*carboxylate* **6e** (0.03 g, 2%) (Found: M^+, 267.1222. $C_{17}H_{17}NO_2$ requires *M*, 267.1254); ν_{max}/cm^{-1} 1715s; λ_{max}/nm (ε) 278 (8400) and 302 (8800); *m*/*z* 267 (M^+, 43%), 252 (38) and 239 (100); δ_H 8.22–8.18 (1 H, m, ArH), 7.30–7.05 (3 H, m, ArH), 6.92 (1 H, s, 2-H), 3.88 (3 H, s, OMe), 2.97–1.12 (6 H, m, 3 × CH_2) and 1.51 (3 H, s, CMe). (ii) The pale yellow band (R_f 0.35) gave a pale yellow oil of *methyl* 1,2,3,10b-*tetrahydro*-10b-*methylpyrrolo*[3,2,1-jk]*carbazole*-4-*carboxylate* **6f** (0.33 g, 25%) (Found: M^+, 267.1255. $C_{17}H_{17}NO_2$ requires *M*, 267.1254); ν_{max}/cm^{-1} 1718s; λ_{max}/nm (ε) 275 (9800) and 285 (9200); *m*/*z* 267 (M^+, 22%), 252 (19) and 239 (100); δ_H 7.62 (1 H, s, H-3), 7.40–6.90 (4 H, m, ArH), 3.81 (3 H, s, OMe), 2.98–0.96 (6 H, m, 3 × CH_2) and 1.48 (3 H, s, CMe). (iii) The violet band (R_f 0.20) gave black needles of *dimethyl* 1,2,3,12b-*tetrahydro*-12b-*methylazepino*[3,2,1-jk]*carbazole*-5,7-*dicarboxylate* **7b** (0.52 g, 30%); m.p. 163–175 °C (chloroform–methanol) (Found: C, 71.4; H, 6.05; N, 3.95. $C_{21}H_{21}NO_4$ requires C, 71.5; H, 6.0; N, 4.0%); ν_{max}/cm^{-1} 1720s, 1710s and 1660m; λ_{max}/nm (ε) 265 (15 000), 300 (10 000) and 528 (850); *m*/*z* 351 (M^+, 61%) and 336 (100); δ_H 7.26–6.48 (6 H, m, 4 ArH and 2 × olefinic H), 3.77 (3 H, s, OMe), 3.72 (3 H, s, OMe), 2.50–1.25 (6 H, m, 3 × CH_2) and 1.31 (3 H, s, CMe).

X-Ray Crystal Structure Analysis.—Intensity data were measured on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) and scintillation counter; cell parameters by least squares from the setting angles of 25 reflections $10° < 2\theta < 13°$. The ω–2θ scan in the bisect mode was employed, with the scanning extended 25% on each side for background measurement. No decay was observed in the three standard reflections measured every 2 h for each compound. Lorentz and polarization corrections and no absorption correction, was applied. For compound **5b**, 1517 independent reflections with $I > 3\sigma(I)$, where $\sigma(I) = S + 4(B1 + B2)$, *S* = scan, *B*1 and *B*2 = background counts, were considered observed and used. For compound **7b**, 1075 independent reflections with $I > \sigma(I)$, where $\sigma(I) = S + 4(B1 + B2)$, were considered observed and used.

Both structures were determined by direct methods using MULTAN 11/82[26] and refined by full matrix least squares on *F* using atomic scattering factors from International Tables for X-Ray Crystallography (1974) and the Enraf–Nonius SDP-1985 Programs on a MicroVAX II computer. The oxygen, nitrogen and carbon atoms were refined anisotropically and the hydrogen atoms placed in calculated positions were not refined.

Crystal Data for **5b**.—$C_{20}H_{19}NO_3$, *M* = 321.38, monoclinic, space group $P2_1/c$, a = 8.950(2), b = 15.135(2), c = 12.363(1) Å, β = 91.35(1)°, V = 1674.2(1.0) Å^3, Z = 4, D_x = 1.275 g cm^{-3}, μ(Mo-Kα) = 0.80 cm^{-1}, $F(000)$ = 680, T = 298 K, R = 0.039 for 1517 independent reflections with $|F_o| \geqslant 6\sigma(|F_o|)$. A crystal of dimensions 0.3 × 0.4 × 0.5 mm was used for the measurement of diffraction data. Intensity data with $2\theta_{max} = 46°$ in the range $0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 16$, $-13 \leqslant l \leqslant 13$ were measured with ω-scan angle (0.50 + 0.344 tan θ)° at a scan speed of 0.78 to 5.49 deg min^{-1} for 2623 reflections, 2255 measured uniquely and 226 measured twice (R_{int} = 0.017). Convergence for 241 variables by least squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.045F_o^2)^2]$ for reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and w = −ve for all other reflections, was reached at R = 0.039 and wR = 0.045 and S = 1.412 for 1517 reflections with $|F_o| \geqslant 6\sigma(|F_o|)$. $(\Delta/\sigma)_{max}$ = 0.02. A final difference Fourier was featureless, with maximum positive and negative peaks of 0.15 and 0.19 e Å^{-3} respectively. Atomic coordinates, bond distances and bond angles together with other crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

Crystal Data for Compound **7b**.—$C_{21}H_{21}NO_4$ *M* = 351.41, orthorhombic, space group $P2_12_12_1$, a = 8.288(1), b = 13.254(3), c = 16.193(3) Å, V = 1778.9(1.0) Å^3, Z = 4, D_x = 1.312 g cm^{-3}, μ(Mo-Kα) = 0.85 cm^{-1}, $F(000)$ = 744, T = 297 K, R = 0.039 for 1075 independent reflections with $|F_o| \geqslant 2\sigma(|F_o|)$. A crystal of dimensions 0.2 × 0.25 × 0.3 mm was used for the measurement of diffraction data. Intensity data with $2\theta_{max} = 48°$ in the range $0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 15$, $-18 \leqslant l \leqslant 18$ were measured with ω-scan angle (0.60 + 0.344 tan θ)° at a scan speed of 0.66 to 5.49 deg min^{-1} for 3642 reflections, 8 unique and 3634 measured twice (R_{int} = 0.028). Convergence for 235 variables by least squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.04F_o^2)^2]$ for reflections with $F_o^2 \geqslant \sigma(F_o^2)$ and w = −ve for all other reflections, was reached at R = 0.039 and wR = 0.036 and S = 1.012 for 1075 reflections with $|F_o| \geqslant 2\sigma(|F_o|)$. $(\Delta/\sigma)_{max}$ = 0.05. A final difference Fourier map was featureless, with maximum positive and negative peaks of 0.14 and 0.18 e Å^{-3} respectively. Atomic coordinates, bond distances and bond angles together with other crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.*

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* For full details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, issue 1.

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