Indole β-Nucleophilic Substitution. Part 5.[1] Synthesis of the Four Isomeric 5*H*-Pyrido[*x*,*y*-*b*]carbazole-5,11-diones and Benzo Analogues

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The four isomeric 6*H*-pyrido[*x*',*y*':5,6]oxepino[3,2-*b*]indol-5(12*H*)-ones were transformed by alkali and air into the title pyridocarbazolequinones. A mechanism is proposed for these transformations.

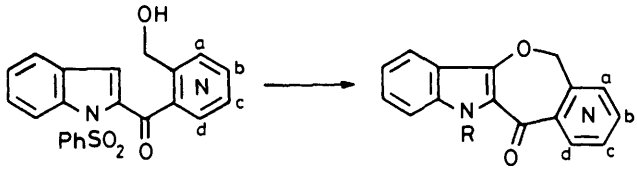
We have described [2] the role of intramolecular indole-β-nucleophilic substitution in the transformation of the four isomeric keto-alcohols (1) into the corresponding pyrido-oxepino-indoles (2). These reactions are efficient and rapid, requiring no more than 5 min in refluxing aqueous methanolic sodium hydroxide in the slowest case. That periods of reflux no longer than the minimum are essential for good yields of (2) became clear during studies of (1c) when after a reaction time of 0.5 h, the initial product (2c) had all but disappeared to be replaced with another product. It was subsequently shown that each of the pyrido-oxepino-indoles could be similarly transformed into a new product. The further transformation was fastest for (2c) (76% after 1 h), next fastest for (2a) (89% after 12 h), with (2b) (46% after 93 h) and (2d) (43% after 33 h) requiring very much longer.

In each case the product was that of oxidation and had two hydrogen atoms less than its pyrido-oxepino-indole precursor. Each oxidation product still had signals for all the aromatic protons, still had an NH signal, but did *not* have a methylene signal. They are assigned quinone structures (3a—d). Quinone (3b) was shown to be identical with a sample of this quinone prepared unambiguously by another route.[3]

Since it was possible to conceive a mechanistic route from (2) to (3) which depended on base removal of the indolic *N*-hydrogen, the *N*-methyl homologue (2e) of the most reactive pyrido-oxepino-indole was prepared, by reaction of (2c) with methyl iodide in the presence of sodium hydride in dimethylformamide; some spiro-ketone (4) was also formed, probably by a light-catalysed process.[4] The N-blocked pyrido-oxepino-indole (2e) was transformed into a quinone, (3e), even more rapidly than was (2c) transformed into (3c).

Rigorous exclusion of oxygen from a solution of (2c) or (2e) in refluxing methanolic alkali led to recovery of starting material. The pyrido-oxepino-indole (2c) was still transformed into quinone under the alkali–oxygen conditions when light was excluded from the reaction. No oxidation was observed when (2c) was heated in 5M-hydrochloric acid in the presence of oxygen, the starting material being recovered. Application of the quinone-forming conditions to the benzoxepino-indole (5a) [5] or the benzoxepino-azaindole (6) [6] brought no change to these compounds over two days. The nitro-derivatives (5b) and (5c) were, however, transformed into nitro-quinones (7a) and (7c), though other products were also formed and these reactions are more fully discussed below. The quinolino-oxepino-indole (8) was smoothly transformed into the quinone (9).

We believe that these results, in particular those which show the quinone-forming process to work best/at all when the methylene hydrogens in the oxepino-indole are acidified (either by a fused pyridine or quinoline ring or by an aromatic nitro-group), can be best rationalised in terms of the mechanism shown in Scheme 1 [illustrated for (2c)]. We envisage the initial anion (10) being in equilibrium with the benzene oxide (11) which is then trapped by interaction with oxygen giving (12) now at the oxidation level of the product quinone.

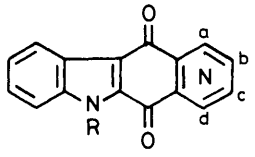


(1)

a; N at a
b; N at b
c; N at c
d; N at d

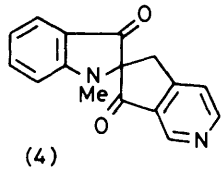
(2) R

a; N at a, H
b; N at b, H
c; N at c, H
d; N at d, H
e; N at c, Me

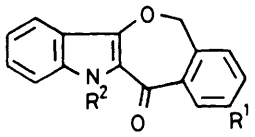


(3) R

a; N at a, H
b; N at b, H
c; N at c, H
d; N at d, H
e; N at c, Me

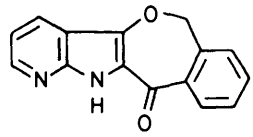


(4)



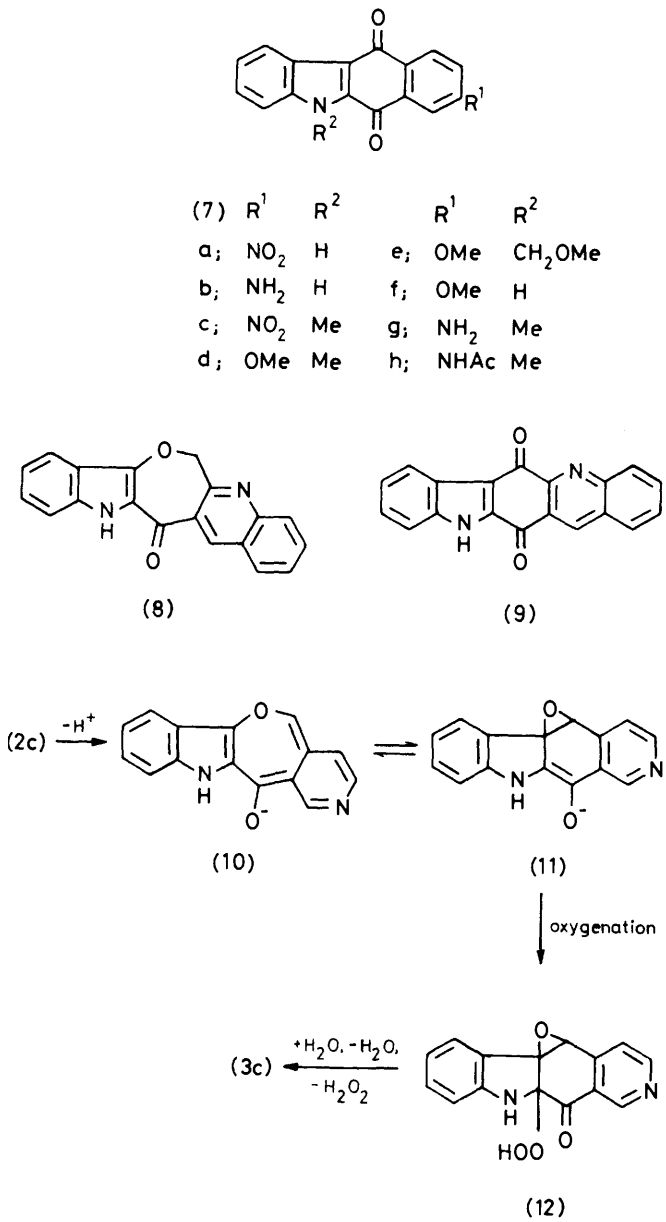
(5) R^1 R^2

a; H H
b; NO_2 H
c; NO_2 Me



(6)

The reaction of nitro-benzoxepino-indole (5b), prepared by an intramolecular indole β-substitution process from the keto-alcohol produced by condensing 1-phenylsulphonylindol-2-yl-lithium with 6-nitroisobenzofuran-1(3*H*)-one,[7] although giving some nitro-quinone (7a) (17%) also produced the amino-quinone (7b) (19%) and considerable quantities of tar. A cleaner reaction was observed with the *N*-methyl-homologue (5c): as well as the nitro-quinone (7c) (21%) the main product now was the methoxy-quinone (7d) in which methoxide had displaced the nitro-group from the activated aromatic ring; the



Scheme 1.

N-methoxymethyl-methoxy-quinone (7e), hydrolysable with dilute acid to the *N*-hydrogen methoxy-quinone (7f), was also isolated. The methoxymethyl group in (7e), one may speculate, arises *via* hydrogen atom abstraction from the *N*-methyl group.

Experimental

General Procedure for Formation of Quinones.—The oxepinoindole (*W* mg) in methanol (*X* ml) and 3M sodium hydroxide (*Y* ml) was heated under reflux with passage of air through the solution for *Z* h. The mixture was poured into water and the crude quinone (A mg) or mixture of quinones filtered off and purified as indicated for each. *Pyrido*[3,2-b]*carbazole*-5,11(6H)-*dione* (3a), $W = 200$, $X = 60$, $Y = 30$, $Z = 12$, $A = 180$, m.p. 365 °C (decomp.) After sublimation (200 °C at 0.1 mmHg), $\lambda_{max.}$ (EtOH–NaOH) 272, 327, and 445 nm (log ε 4.23, 4.16, and 3.75); $\nu_{max.}$ (Nujol) 1 660—1 670br, s cm^{-1}; τ [$(CD_3)_2SO$] 1.0 (1 H, d, *J* 5 Hz, 2-H), 1.52 (1 H, d, *J* 7 Hz, 4-H), 1.75 (1 H, d, *J* 7 Hz, 10-H), 2.20 (1 H, dd, *J* 7, 5 Hz, 3-H), 2.39 (1 H, d, *J* 7 Hz, 7-H), 2.54 (1 H, t, *J* 7 Hz, ArH), and 2.62 (1 H, t, *J* 7 Hz, ArH); *m/z* 248 (M^+, 100%), 220 (65), 192 (22), and 164 (16) (Found: C, 72.3; H, 3.1; N, 11.1. $C_{15}H_8N_2O_2$ requires C, 72.57; H, 3.25; N, 11.3%); pyrido[4,3-*b*]carbazole-5,11-(6*H*)-dione (3b), $W = 200$, $X = 60$, $Y = 30$, $Z = 93$, $A = 90$, m.p. 317—320 °C, shown to be identical with an authentic sample; [3] *pyrido*[3,4-b]*carbazole*-5,11(10H)-*dione* (3c), $W = 200$, $X = 60$, $Y = 30$, $Z = 1$, $A = 150$, m.p. 317—320 °C after sublimation (200 °C at 0.1 mmHg), $\lambda_{max.}$ (EtOH–NaOH) 270, 303, and 450 nm (log ε 4.30, 4.37, and 3.72); $\nu_{max.}$ (Nujol) 1 665 and 1 640s cm^{-1}; τ[$(CD_3)_2SO$] −3.3 (1 H, b, NH), 0.71 (1 H, s, 4-H), 0.85 (1 H, d, *J* 5 Hz, 2-H), 1.75 (1 H, d, *J* 7 Hz, 10-H), 2.00 (1 H, d, *J* 5 Hz, 1-H), 2.34 (1 H, d, *J* 7 Hz, 7-H), 2.48 (1 H, t, *J* 7 Hz, ArH), 2.56 (1 H, t, *J* 7 Hz, ArH); *m/z* 248 (M^+, 100%), 220 (48), 192 (19), and 164 (18) (Found: C, 72.5; H, 3.2; N, 11.6. $C_{15}H_8N_2O_2$ requires C, 72.57; H, 3.25; N, 11.29%); *pyrido*[2,3-b]*carbazole*-5,11-(10H)-*dione* (3d), $W = 210$, $X = 60$, $Y = 30$, $Z = 33$, $A = 90$, m.p. 315—319 °C after sublimation (200 °C at 0.1 mmHg), $\lambda_{max.}$ (EtOH) 214, 230, 270, and 394 nm (log ε 4.39, 4.22, 4.25, and 3.66); $\nu_{max.}$ (Nujol) 1 675s and 1 650s cm^{-1}; τ[$(CD_3)_2SO$] −3.2 (1 H, s, NH), 1.05 (1 H, d, *J* 5 Hz, 3-H), 1.55 (1 H, d, *J* 7 Hz, 1-H), 1.82 (1 H, d, *J* 7 Hz, 10-H), 2.18 (1 H, dd, *J* 7,5 Hz, 2-H), 2.42 (1 H, d, *J* 7 Hz, 7-H), 2.55 (1 H, t, *J* 7 Hz, ArH), and 2.64 (1 H, t, *J* 7 Hz, ArH); *m/z* 248 (M^+, 100%), 220 (36), 192 (21), and 164 (11) (Found: C, 72.7; H, 3.1; N, 11.2. $C_{15}H_8N_2O_2$ requires C, 72.57; H, 3.25; N, 11.29%); 10-*methyl-pyrido*[3,4-b]*carbazole*-5,11(10H)-*dione* (3e), $W = 30$, $X = 3$, $Y = 1.5$, $Z = 0.5$, $A = 21$, m.p. 195—225 °C, $\lambda_{max.}$ (EtOH) 250, 280, and 390 nm; $\nu_{max.}$ ($CHCl_3$) 1 720bm and 1 660s cm^{-1}; τ($CDCl_3$) 0.54 (1 H, s, 4-H), 0.90 (1 H, d, *J* 5 Hz, 2-H), 1.50 (1 H, d, *J* 7 Hz, 10-H), 1.92 (1 H, d, *J* 5 Hz, 1-H), 2.44 (1 H, d, *J* 7 Hz, 7-H), 2.52 (1 H, t, *J* 7 Hz, ArH), 2.64 (1 H, t, *J* 7 Hz, ArH), and 5.69 (3 H, s, NMe); *m/z* 262 (M^+, 100%), 234 (22), and 206 (20) [Found (by mass spectrometry): *M*, 262.074. $C_{16}H_{10}N_2O_2$ requires *M*, 262.974]; 8-*nitrobenzo*[b]*carbazole*-6,11(5H)-*dione* (7a) and 8-*aminobenzo*[b]*carbazole*-6,11(5*H*)-*dione* (7b), $W = 100$, $X = 15$, $Y = 7.5$, $Z = 48$, $A = 58$; the mixture was extracted with THF, the solvent removed and the residue crystallised twice from acetic acid and then sublimed to give (7a), $A = 18$, m.p. 290—295 °C, with sublimation $\lambda_{max.}$ (EtOH) 212, 253, 299, and 404 nm (log ε 4.56, 4.45, 4.29, and 3.64); $\nu_{max.}$ (Nujol) 3 240s, 1 650s, and 1 635s cm^{-1}; τ [$(CD_3)_2SO$] 1.26 (1 H, s, 7-H), 1.31 (1 H, d, *J* 8 Hz, 9-H), 1.61 (1 H, d, *J* 8 Hz, 10-H), 1.72 (1 H, d, *J* 8 Hz, 1-H), 2.32 (1 H, d, *J* 8 Hz, 4-H), 2.46 (1 H, t, *J* 8 Hz, ArH), 2.55 (1 H, t, *J* 8 Hz, ArH), and 3.60 (1 H, s, NH); *m/z* 292 (M^+, 100%), 262 (12), 246 (22), 234 (5), and 218 (18) (Found: C, 65.5; H, 2.7; N, 9.3. $C_{16}H_8N_2O_4$ requires C, 65.8; H, 2.7; N, 9.6%); the mother liquor from the first crystallisation was evaporated and the residue sublimed to give $\lambda_{max.}$ (EtOH) 215, 235, 258, 291, 380, and 502 nm (log ε 4.40, 4.30, 4.37, 4.53, 4.09, and 3.15); $\nu_{max.}$ (Nujol) 3 460m, 3 320m, 3 240s, 1 650, and 1 615s cm^{-1}; τ [$(CD_3)_2SO$] 1.78 (1 H, d, *J* 9 Hz, 1-H), 2.13 (1 H, d, *J* 9 Hz, 4-H), 2.38 (1 H, d, *J* 9 Hz, 10-H), 2.57 (1 H, t, *J* 9 Hz, 9-H), 2.62 (1 H, s, 7-H), 2.66 (1 H, t, *J* 9 Hz, ArH), and 3.01 (1 H, d, *J* 9 Hz, ArH), *m/z* 262 (M^+, 100%), 234 (20), and 205 (13) [Found: C, 72.8; H, 3.8; N, 10.0%; *M* (by mass spectrometry), 262.074. $C_{16}H_{10}N_2O_2$ requires C, 73.3; H, 3.8; N, 10.7%; *M*, 262.074]; 5-*methyl*-8-*nitrobenzo*[b]*carbazole*-6,11(5H)-*dione* (7c), 8-*methoxy*-5-*methylbenzo*[b]*carbazole*-6,11(5H)-*dione* (7d), and 8-*methoxy*-5-*methoxymethylbenzo*[b]*carbazole*-6,11(5H)-*dione* (7e), $W = 1\,000$, $X = 200$, $Y = 100$, $Z = 36$, $A = 920$, oily solid which was extracted into THF, the solvent evaporated, and the residue crystallised from glacial acetic acid four times,

then sublimed to give (7c), A = 210, m.p. 288—291 °C, $\lambda_{max.}$ (EtOH) 209, 252sh, 257, 270sh, 291sh, 337sh, 394sh, and 438sh nm (log ε 4.48, 4.45, 4.47, 4.40, 4.29, 3.85, 3.78, and 3.56); $\nu_{max.}$ (Nujol) 1 665s and 1 650s cm^{-1}; τ($CDCl_3$) 0.97 (1 H, s, 7-H), 1.42 (1 H, d, J 8 Hz, 9-H), 1.50 (1 H, d, J 8 Hz, 10-H), 1.55 (1 H, d, J 8 Hz, 1-H), 2.44 (1 H, d, J 8 Hz, 4-H), 2.45 (1 H, t, J 8 Hz, ArH), 2.52 (1 H, t, J 8 Hz, ArH), and 5.65 (3 H, s, NMe); m/z 306 (M^+, 100%), 260 (17), 248 (4), and 232 (8) (Found: C, 66.9; H, 3.24; N, 8.9%. $C_{17}H_{10}N_2O_4$ requires C, 66.7; H, 3.27; N, 9.15%).

The mother liquor from the first crystallisation was evaporated and the residue crystallised from chloroform twice, then sublimed to give (7d) A = 350, m.p. 204—206 °C, $\lambda_{max.}$ (EtOH) 211, 220sh, 270, 280, 304sh, 353, 382sh, and 440sh nm (log ε, 4.39, 4.19, 4.44, 4.44, 3.80, 3.89, 3.67, and 3.23), $\nu_{max.}$ (Nujol) 1 660s and 1 640s cm^{-1}; τ ($CDCl_3$) 1.52 (1 H, d, J 8 Hz, 9-H), 1.82 (1 H, d, J 9 Hz, 10-H), 2.36 (1 H, s, 7-H), 2.46—2.62 (3 H, m, ArH), 2.80 (1 H, d, J 9 Hz, ArH), 5.77 (3 H, s, OMe), and 6.04 (3 H, s, NMe); m/z 291 (M^+, 100%), 262 (7), 248 (13), 234 (2), and 220 (7) (Found: C, 74.0; H, 4.6; N, 4.4%. $C_{18}H_{13}NO_3$ requires C, 74.2; H, 4.5; N, 4.8%); the mother liquor from crystallisation of (7d) was evaporated and a sample (10 mg) purified by p.l.c., eluting 5 times with toluene, to give (7e) A = 140, m.p. 156—160 °C (from chloroform), $\lambda_{max.}$ (EtOH) 212, 221sh, 272sh, 276, 304sh, 355, 382sh, and 440sh nm (log ε 4.28, 4.03, 4.43, 4.45, 3.62, 3.85, 3.51, and 2.68); $\nu_{max.}$ (Nujol) 1 650s and 1 635s cm^{-1}; τ ($CDCl_3$) 1.48 (1 H, d, J 8 Hz, 9-H), 1.80 (1 H, d, J 8 Hz, 10-H), 2.33 (1 H, s, 7-H), 2.34 (1 H, d, J 8 Hz, 1-H), 2.47 (1 H, t, J 8 Hz, ArH), 2.55 (1 H, t, J 8 Hz, ArH), 2.78 (1 H, d, J 8 Hz, ArH), 3.82 (2 H, s, CH_2OMe), 6.03 (3 H, s, OMe), and 6.61 (3 H, s, NMe); m/z 321 (M^+ 55%), 306 (63), 290 (20), and 278 (59) [Found (by mass spectrometry); M, 321.099. $C_{19}H_{15}NO_4$ requires M, 321.100]; *benz*[2,3]*indolo*[5,6-b]*quinoline*-6,13(5H)-*dione* (9), W = 60, X = 200, Y = 30, Z = 10, A = 45, m.p. 153—158 °C (from methanol), $\lambda_{max.}$ (EtOH) 228sh, 270sh, 285, 288sh, 323sh, 327sh, 344sh, 350, and 390 (log ε 4.63, 4.24, 4.26, 4.25, 4.11, 4.06, 3.82, 3.78, and 3.61); $\nu_{max.}$ (Nujol) 3 300m, 1 628s, and 1 615s cm^{-1}; τ [$(CD_3)_2SO$] 1.36 (1 H, s, 14-H), 1.76 (1 H, d, J 9 Hz, ArH), 1.9—2.1 (2 H, m, ArH), 2.28—2.46 (4 H, m, ArH), 2.66 (1 H, t, J 7 Hz, ArH), 4.72 (1 H, bs); m/z 298 (M^+, 100%), 270 (33), and 242 (28) (Found: C, 76.2; H, 3.1; N, 9.6%. $C_{19}H_{10}N_2O_2$ requires C, 76.5; H, 3.4; N, 9.4%).

11-*Methylpyrido*[3′,4′:5,6]*oxepino*[3,2-b]*indol*-12(5H,11H)-*one* (2e) *and* 1′-*Methylspiro*[*cyclopenta*[c]*pyridine*-6(7H),2′(3′H)-*indole*]-3′,7-*dione* (4).—The oxepinoindole (2c) (100 mg) in dry DMF (1 ml) was treated first with a slurry of sodium hydride (9.6 mg) in DMF (1 ml) under nitrogen at 0 °C and then after 15 min with methyl iodide (57 mg). After a further 3 h at 0 °C the mixture was poured into water (50 ml) and extracted with ether. The total organic material (98 mg) was purified by preparative layer chromatography [silica, EtOAc–PhMe (1 : 1)] to give the N_a-methyl quinone (3e) (7 mg) (R_F 0.5), the N_a-*methylpyrido-oxepinoindole* (2e) (60 mg) (R_F 0.35), m.p. 160—170 °C, $\lambda_{max.}$ (EtOH) 215, 250sh, 338, and 400 nm; $\nu_{max.}$ 1 610s cm^{-1}; τ ($CDCl_3$), 0.7 (1 H, s, 1-H), 1.20 (1 H, d, J 5 Hz, 3-H), 2.24 (1 H, d, J 8 Hz, 10-H), 2.55 (1 H, d, J 8 Hz, 7-H), 2.65 (2 H, m, ArH), 2.85 (1 H, t, J 8 Hz, ArH), 4.75 (2 H, s, OCH_2), and 5.85 (3 H, s, NMe), m/z 264 (M^+, 80%), 235 (100) 221 (42), 207 (24), 76 (22) [Found (by mass spectrometry): M, 264.090. $C_{16}H_{12}N_2O_2$ requires M, 264.089], and the *spiro-ketone* (4) (23 mg) (R_F 0.2) as a red gum, $\lambda_{max.}$ (EtOH) 305, 415, and 500 nm; $\nu_{max.}$ ($CHCl_3$) 1 730s, 1 695s, and 1 620m cm^{-1}; τ ($CDCl_3$) 0.95 (1 H, s, py-α-H), 1.15 (1 H, d, J 5 Hz, py-α-H), 2.3—2.8 (3 H, m, ArH), 3.02 (1 H, d, J 7 Hz, indole-4-H), 3.15 (1 H, t, J 7 Hz, ArH), 6.42 (1 H, d, J 17 Hz, CH_AHB), 6.66 (1 H, d, J 17 Hz, CH_AH_B), and 7.04 (3 H, s, NMe); m/z 264 (M^+, 41%), 235 (62), and 94 (100) [Found (by mass spectrometry): M, 264.090. $C_{16}H_{12}N_2O_2$ requires M, 264.089].

2-*Hydroxymethyl*-5-*nitrophenyl* 1-*Phenylsulphonylindol*-2-*yl Ketone*.—To 1-phenylsulphonylindol-2-yl-lithium [from 1-phenylsulphonylindole (7.18 g) in THF (150 ml) and n-butyl-lithium (20 ml; 1.55M solution in hexane)] was added at −78 °C a slurry of 6-nitroisobenzofuran-1(3*H*)-one [5] (5.01 g) in THF (150 ml). The mixture was allowed to come to room temperature, and stirred for a further 1 h. The solvent was evaporated and the residue partitioned between water and ethyl acetate. The dried organic phase on evaporation gave an orange oil purified by chromatography over silica when ether eluted the pure *keto-alcohol* (4.42 g), m.p. 92—95 °C (from methanol), $\lambda_{max.}$ (EtOH) 242, 271sh, 290sh, and 364sh nm (log ε 4.20, 3.95, 3.89, and 2.84); $\nu_{max.}$ (Nujol) 3 350s, 1 665, and 1 640s cm^{-1}; τ ($CDCl_3$) 1.56 (1 H, d, J 9 Hz, ArH), 1.67 (1 H, s, ArH), 1.82 (1 H, d, J 9 Hz, ArH), 2.00—2.08 (2 H, m, ArH), 2.32—2.52 (6 H, m, ArH), 2.61 (1 H, t, J 8 Hz, ArH), 2.85 (1 H, s, indole-3-H), 5.03 (2 H, s, CH_2O), and 6.50—6.80 (1 H, bs, exchangeable, OH); m/z 436 (M^+, 0.5%), 418 (1), 295 (9), 277 (7), 179 (16), and 77 (100) (Found: C, 60.4; H, 3.65; N, 6.3. $C_{22}H_{16}N_2O_6S$ requires C, 60.55; H, 3.7; N, 6.4%).

9-*Nitro*[2]*benzoxepino*[4,3-b]*indol*-11(6H,12H)-*one* (5b).—2-Hydroxymethyl-5-nitrophenyl 1-phenylsulphonylindol-2-yl ketone (1.12 g) was heated in refluxing methanol (30 ml) with aqueous 3M-sodium hydroxide (15 ml) for 5 min. The orange precipitate was filtered off from the cooled solution to give the *oxepinoindole* (5b) (0.66 g), m.p. 297—300 °C (from methanol), $\lambda_{max.}$ (EtOH) 250, 262sh, and 343 nm (log ε 4.13, 4.01, and 3.98); $\nu_{max.}$ (Nujol) 3 300m and 1 610s cm^{-1}; τ ($CDCl_3$) 1.28 (1 H, s, 10-H), 1.46 (1 H, d, J 9 Hz, 8-H), 2.00 (2 H, m, ArH), 2.30 (1 H, d, J 9 Hz, ArH), 2.60 (2 H, m, ArH), 2.92 (1 H, t, J 7 Hz, ArH), and 4.45 (2 H, s, CH_2O); m/z 294 (M^+ 100%), 277 (16), 265 (18), 220 (30), and 193 (2) (Found: C, 65.2; H, 3.4; N, 9.3%. $C_{16}H_{10}N_2O_4$ requires C, 65.3; H, 3.4; N, 9.5%).

12-*Methyl*-9-*nitro*[2]*benzoxepino*[4,3-b]*indol*-11(6H,12H)-*one* (5c).—To a vigorously stirred solution of the oxepinoindole (5b) (3.08 g) in THF (150 ml) containing tetrabutylammonium hydroxide (40% w/w/ solution; 15 drops), was added aqueous sodium hydroxide (50%; 150 ml). After 5 min methyl iodide (60 ml) was added, in 3-ml portions during 45 min. The THF was evaporated off under reduced pressure and the residue partitioned between water and chloroform. The chloroform layer was dried and evaporated to leave the *oxepinoindole* (5c) as an orange crystalline material (2.76 g), m.p. 243—245 °C (from toluene), $\lambda_{max.}$ (EtOH) 225, 246, 337, and 406 nm (log ε 4.30, 4.32, 4.20, and 3.70); $\nu_{max.}$ (Nujol) 1 617s cm^{-1}; τ ($CDCl_3$) 1.06 (1 H, s, 10-H), 1.58 (1 H, d, J 9 Hz, 8-H), 2.26 (1 H, d, J 8 Hz, 13-H), 2.37 (1 H, d, J 9 Hz, 16-H), 2.53 (1 H, t, J 8 Hz, ArH), 2.64 (1 H, d, J 8 Hz, ArH), 2.87 (1 H, t, J 8 Hz, ArH), 4.67 (2 H, s, CH_2O), and 5.89 (3 H, s, NMe); m/z 308 (M^+, 100%) 291 (4), 279 (84), 265 (13), and 233 (54) (Found: C, 65.9; H, 3.8; N, 8.8%. $C_{17}H_{12}N_2O_2$ requires C, 66.2; H, 3.9; N, 9.1%).

2-*Hydroxymethylquinolin*-3-*yl* 1-*Phenylsulphonylindol*-2-*yl Ketone*.—To 2-lithiophenylsulphonylindole [from phenylsulphonyl indole (1.58 g) in THF (150 ml) and n-butyl-lithium (6.7 ml; 1.55M solution in hexane)] was added at −78 °C a slurry of 2-hydroxymethylquinoline-3-carboxylic acid lactone [8] (0.7 g) in THF (50 ml). The mixture was allowed to come to room temperature when the solvent was evaporated and the residue partitioned between water and ethyl acetate. The

dried organic phase on evaporation gave a foam purified by chromatography (silica, EtOAc–PhMe 1 : 1) to give the pure *keto-alcohol* (1.03 g), m.p. 181—84 °C (from methanol), $\lambda_{max.}$ (EtOH) 230sh, 250sh, 253, and 295 nm (log ε 4.56, 4.58, 4.59, and 4.33), $\nu_{max.}$ (Nujol) 3 390m and 1 670s cm^{-1}; τ ($CDCl_3$) 1.58 (1 H, s, py-γ-H), 1.83 (2 H, d, *J* 8 Hz, ArH), 2.0 (2 H, m, ArH), 2.37—2.56 (5 H, m, ArH), 2.67 (1 H, t, *J* 7 Hz, ArH), 2.97 (1 H, s, indole-3-H), 4.70 (2 H, s, CH_2O), and 4.90 (1 H, s, OH); *m/z* 442 (M^+, 2%), 424 (4), 301 (100), 283 (72), and 185 (32) (Found: C, 67.5; H, 4.1; N, 6.1. $C_{25}H_{18}N_2SO_4$ requires C, 67.9; H, 4.0; N, 6.3%).

Indolo[6,7-b]*oxepino*[3,4-b]*quinolin*-13(6H,12H)-*one* (8).—2-Hydroxymethylquinolin-3-yl 1-phenylsulphonylindol-2-yl ketone (300 mg) was heated in refluxing methanol (30 ml) with aqueous 3M-sodium hydroxide (10 ml) for 10 min. The yellow precipitate was filtered off from the cooled solution and recrystallised from methanol to give the *oxepinoquinoline* (8) (200 mg), m.p. 270—271 °C, $\lambda_{max.}$ (EtOH) 255, 344, and 418sh nm (log ε 4.31, 4.13, and 3.52); $\nu_{max.}$ (Nujol) 3 300m and 1 630s cm^{-1}; τ [$(CD_3)_2SO$] 0.94 (1 H, s, 14-H), 1.70 (1 H, d, *J* 8 Hz, 11-H), 1.84 (1 H, d, *J* 7 Hz, 6-H), 2.60 (1 H, t, *J* 7 Hz, ArH), 2.22—2.62 (4 H, m, ArH), 2.94 (1 H, t, *J* 7 Hz, ArH), and 6.38 (2 H, s, CH_2O); *m/z* 300 (M^+, 100%), 271 (5), and 243 (7) (Found: C, 75.7; H, 4.1; N, 9.0. $C_{19}H_{12}N_2O_2$ requires C, 76.0; H, 4.0; N, 9.3%).

8-*Methoxybenzo*[b]*carbazole*-6,11(5H)-*dione* (7f).—A solution of the ether (7e) (2 mg) in hydrochloric acid (5M; 2 ml) and methanol (2 ml) was refluxed for 18 h. All solvents were removed and the residue partitioned between water and chloroform. The organic phase was dried and evaporated to give the *quinoline* (7f) as yellow crystals (1 mg), m.p. 160—165 °C (from methanol), $\lambda_{max.}$ (EtOH) 212, 221sh, 272sh, 276, 304sh, and 355 nm (log ε 4.26, 4.07, 4.33, 4.35, 3.71, 3.80, 3.55, and 3.19), τ ($CDCl_3$) 0.56 (1 H, bs, NH), 1.48 (1 H, d, *J* 8 Hz, 10-H), 1.70 (1 H, d, *J* 8 Hz, 1-H), 2.26 (1 H, s, 7-H), 2.40 (1 H, t, *J* 8 Hz, ArH), 2.46 (1 H, d, *J* 8 Hz, 4-H), 2.53 (1 H, t, *J* 8 Hz, ArH), 2.70 (1 H, d, *J* 8 Hz, 9-H), and 5.99 (3 H, s, OMe), *m/z* 277 (M^+, 100%), 248 (8), 234 (15), and 206 (11) [Found (by mass spectrometry): *M*, 277.0742. $C_{17}H_{11}NO_3$ requires *M*, 277.074].

8-*Amino*-5-*methylbenzo*[b]*carbazole*-6,11(5H)-*dione* (7g).—The nitroquinone (7c) (20 mg) in suspension in glacial acetic acid (50 ml) was shaken under an atmosphere of hydrogen at atmospheric pressure and room temperature, with platinum oxide (5 mg) for 24 h. The resultant solution was filtered through Celite and evaporated to give the *amine* (7g) as a red-brown solid (17 mg), m.p. 272—275 °C with sublimation (from glacial acetic acid), $\lambda_{max.}$ (EtOH) 213, 228sh, 278sh, 290, 310-sh, 374, and 500 nm (log ε 4.23, 4.08, 4.18, 4.28, 4.04, 3.79, and 2.90), $\nu_{max.}$ (Nujol) 3 380m, 3 330m, 1 650s, and 1 620s cm^{-1}; τ [$(CD_3)_2SO$] 1.76 (1 H, d, *J* 7 Hz, 10-H), 2.26 (1 H, d, *J* 7 Hz, 1-H), 2.30 (1 H, d, *J* 7 Hz, 4-H), 2.55 (1 H, t, *J* 7 Hz, ArH), 2.68 (1 H, t, *J* 7 Hz, ArH), 2.80 (1 H, s, 7-H), 3.22 (1 H, d, *J* 7 Hz, 9-H), 3.64 (2 H, s, NH_2), and 5.88 (3 H, s, NMe); *m/z* 276 (M^+, 14%), 247 (3), and 224 (8) [Found (by mass spectrometry): *M*, 276.089. $C_{17}H_{12}N_2O_2$ requires *M*, 276.089].

8-*Acetamido*-5-*methylbenzo*[b]*carbazole*-6,11(5H)-*dione* (7h).—The nitro-quinone (7c) (5 mg) in suspension in a mixture of glacial acetic acid (15 ml) and acetic anhydride (15 ml), containing platinum oxide (3 mg) was shaken under hydrogen for 4 h at atmospheric pressure and room temperature. The resultant solution was filtered through Celite and evaporated to give the *acetamide* (7h) as a red-brown solid (4.5 mg), m.p. 318—322 °C (dec.) (from glacial acetic acid), $\lambda_{max.}$ (EtOH) 216, 280sh, 286, 296sh, 307sh, 354, and 424sh nm (log ε 3.97, 4.09, 4.15, 3.95, 3.70, 3.56, and 3.25), $\nu_{max.}$ (Nujol) 3 320s, 1 680s, 1 655s, and 1 630s cm^{-1}; τ (DMSO) 1.66 (1 H, s, 7-H), 1.72 (1 H, d, *J* 8 Hz, 10-H), 1.98 (1 H, d, *J* 8 Hz, 1-H), 2.0 (2 H, d, *J* 8 Hz, 4-H), 2.23 (1 H, d, *J* 8 Hz, 9-H), 2.50 (1 H, t, *J* 8 Hz, ArH), 2.61 (1 H, t, *J* 8 Hz, ArH), 5.83 (3 H, s, NMe), and 7.92 (3 H, s, CH_3CO), *m/z* 318 (M^+, 35%) 291 (5), 276 (60), and 247 (16) [Found (by mass spectrometry); *M*, 318.100. $C_{19}H_{14}N_2O_3$ requires *M*, 318.100].

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