Pyrolysis of Quinoline-3,4-dicarboxylic Anhydrides Bearing 2-Phenyl, 2-Benzyl and 2-*o*-Tolyl Substituents: Formation of Products of Carbene Insertion and Addition[†]

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Abstract

Flash vacuum pyrolysis of 2-phenylquinoline-3,4-dicarboxylic anhydride at 800°/0.06 mm gave indeno[1,2-*b*]indole (30-40%), which readily added nucleophiles Y⁻ at C-10 to give 5,10-dihydro derivatives (Y = H, Me, Ph, NEt₂, OMe, CH(COOMe)₂ and CMe₂NO₂). Similar pyrolysis of the 2-benzylquinoline anhydride gave a 1:2 mixture of the (expected) linear 5*H*-benzo[*b*]carbazole and the (unexpected) angular 7*H*-benzo[*c*]carbazole. The isomeric 2-*o*-tolylquinoline anhydride on similar pyrolysis gave mainly 11*H*-benzo[*a*]carbazole (85%), isomeric benzocarbazoles (4%) and 11*H*-indeno[1,2-*b*]quinoline (2.6%). Most of these products are probably derived from exocyclic carbenes formed by aryne - carbene equilibration, but the last compound may be formed by direct aryne - methyl interaction.

We have shown that the formation of cyclopent[*c,d*]indene on flash vacuum pyrolysis (FVP) of 8-methylnaphthalene-1,2-dicarboxylic anhydride[1] is best interpreted as being due to equilibration of 8-methyl-1,2-naphthalyne with the corresponding exocyclic carbene, followed by carbene insertion into the methyl group.[1,2] In this paper we report the effect of placing phenyl, benzyl or *o*-tolyl groups at C-2 of the related quinoline-3,4-dicarboxylic anhydride precursor.

FVP of 2-Phenylquinoline-3,4-dicarboxylic Anhydride (3) [3]

The corresponding napthalene system, 3-phenylnaphthalene-1,2-dicarboxylic anhydride (1), on FVP at 960°/0.04 mm gives indeno[2, 1-*a*]indene (4) in 95% yield.[4] The 2-phenylquinoline anhydride (2) was prepared by treatment of the known diacid,[5] formed from isatin and ethyl benzoylacetate, with Ac₂O. FVP of the anhydride (2) at 800°/0.06 mm gave a red pyrolysate (30-40% as C₁₅H₉N) on the cold finger condenser which was essentially pure indeno[1,2-*b*]indole (5) but which darkened and decomposed on manipulation in air. High resolution mass spectrometry confirmed the formula C₁₅H₉N, and other spectra (IR, UV, ¹H NMR and ¹³C NMR) were obtained by avoiding or minimizing exposure to the atmosphere. The ¹H NMR spectrum showed a complex aromatic region δ 7.19-6.69 (8H) and a sharp singlet, δ 6.41, for the unique H-10.

The behaviour of the quinoline system (2) closely parallels that of the naphthalene system (1) except for the lower yield, which was associated with the formation of dark material on the exit glassware and carbon in
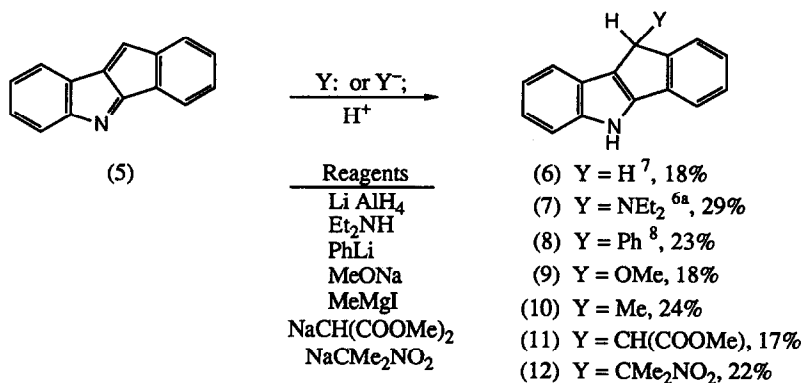
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the tube. In both cases the chemistry can be summarised as in Scheme 1, with the products (4) and (5) being formed by carbene insertion into the aryl-H bond of intermediate (3)

(1) X = CH
(2) X = N

(3)

(4) X = CH
(5) X = N
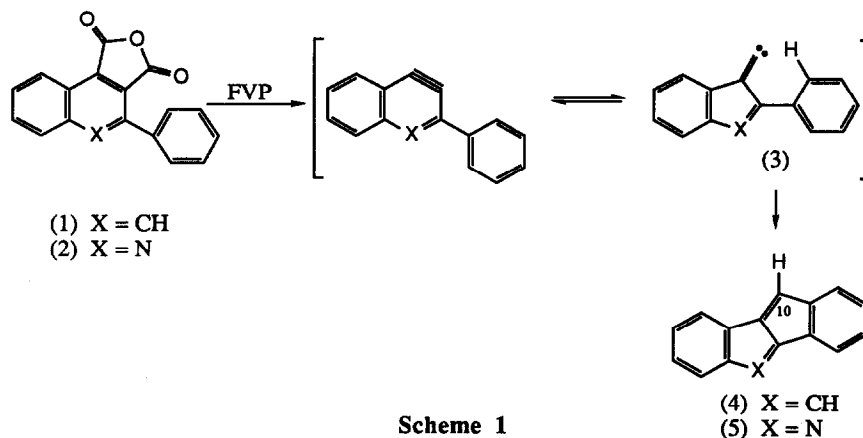
Scheme 1

Previous attempts to make indeno[1,2-*b*]indole by conventional dehydrogenation or elimination methods in solution were unsuccessful[6] and some of these failures may have been due to high reactivity of the electrophilic centre at C-10 of (5). For example, mere dissolution of (5) in MeOH produced a series of ill-defined oligomers, $H(C_{15}H_9N)_n$ OMe (mass spectrometry). To explore the chemistry of indeno[1,2-*b*]indole we added reagents directly to the red pyrolysate from (2). Hydrogenation over 10% Pd/C in ether gave the known 5,10-dihydro compound[7] (10% from anhydride 2), but the yield was better (18%) by reduction with $LiAlH_4$ in ether. The addition of six further varied nucleophiles to C-10 is shown in Scheme 2. Compounds (9) - (11) decomposed on attempted purification and were characterized spectroscopically; there was a problem in the identification of the 10-phenyl compound (8), m.p. 177-178° (dec.) (by Fischer synthesis)[8] and 176-177° (dec.) (from 5 and PhLi). Eisch and Abraham[8] gave m.p. 228-230°, and we cannot at present explain this discrepancy.

(5)

$$\xrightarrow[H^+]{Y; \text{ or } Y^-;}$$

Reagents
Li AlH$_4$
Et$_2$NH
PhLi
MeONa
MeMgI
NaCH(COOMe)$_2$
NaCMe$_2$NO$_2$

(6) Y = H [7], 18%
(7) Y = NEt$_2$ [6a], 29%
(8) Y = Ph [8], 23%
(9) Y = OMe, 18%
(10) Y = Me, 24%
(11) Y = CH(COOMe), 17%
(12) Y = CMe$_2$NO$_2$, 22%

Scheme 2 Yields are based on anhydride (2)

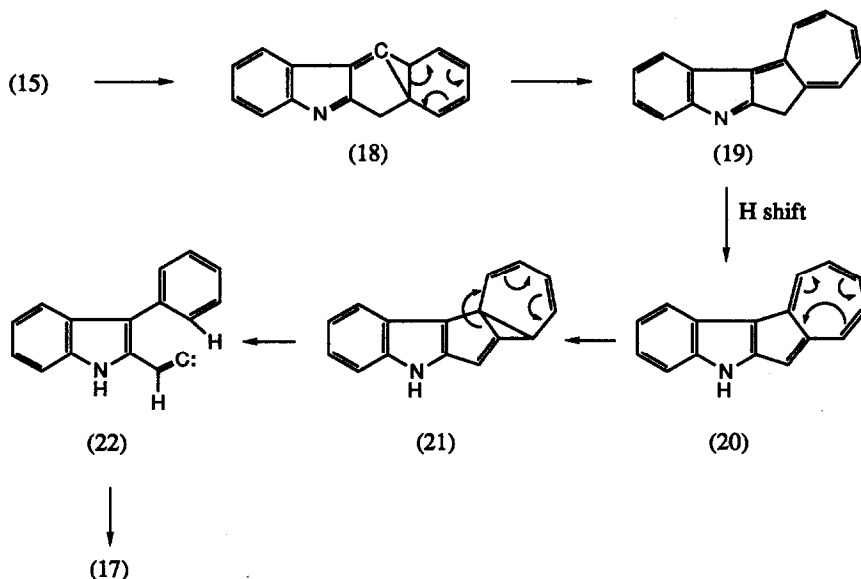## FVP of 2-Benzylquinoline-3,4-dicarboxylic Anhydride (13)

The dicarboxylic acid required for the preparation of 2-benzylquinoline-3,4-dicarboxylic anhydride (13) was made by Pfitzinger condensation of isatin with methyl 4-phenyl-3-oxobutanoate[9] in 30% aqueous KOH. Treatment of the diacid with Ac$_2$O at 100° afforded the yellow crystalline anhydride (13), m.p. 144-145°. On FVP at 800°/0.03 mm anhydride (13) gave a red pyrolysate (104% yield as C$_{16}$H$_{11}$N) which on radial chromatography on silica gel yielded the linear 5H-benzo[b]carbazole (16) and the angular 7H-benzo[c]carbazole (17) in the ratio 1:2 (Scheme 3).

The formation of the linear benzocarbazole (16) by equilibration of the aryne (14) with the exocyclic carbene (15), and insertion of the carbene centre into a neighbouring Ar-H, was expected by analogy with the behaviour of the 2-phenylquinoline system (2→4). The formation of the major angular product, 7H-benzo[c]carbazole (17), did not, however, fit easily into this scheme. We first showed that the angular isomer (17) is *not* a secondary isomerization product of the linear isomer (16); although (16) showed up to 50% decomposition on FVP at 800°, no angular isomer (17) was formed.
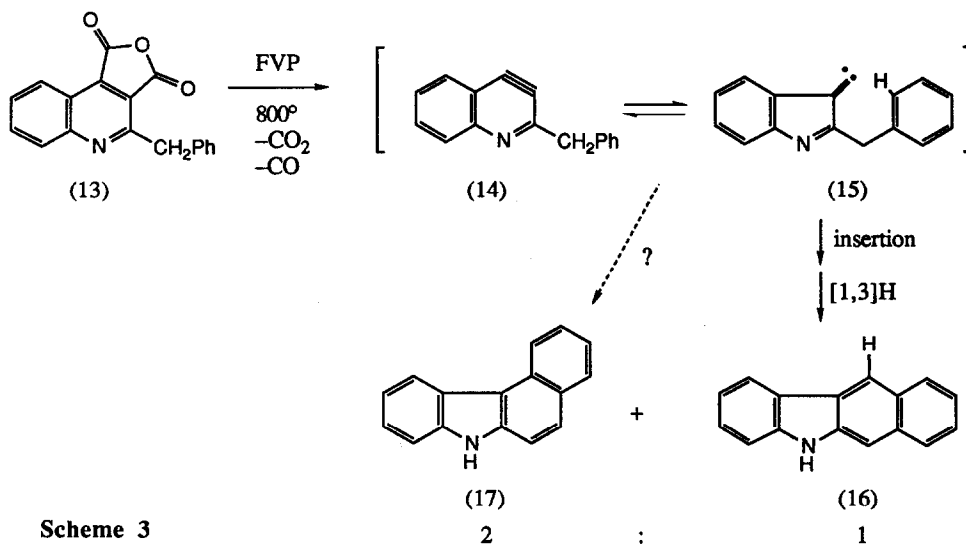
Scheme 3

The formation of the angular product (17) can be rationalised by invoking an initial *addition* of the carbene centre in (15) to the neighbouring aromatic ring, but the subsequent pathway is speculative and long (Scheme 4). The initial adduct (18) should reasonably undergo electrocyclic ring expansion to give (19). *H*-Migration to form the indole system in (20) also forms the isomeric terminal cycloheptatriene ring. Electrocyclic ring contraction of this ring would lead to the pentacyclic system (21), analogous to the initial adduct (18), and elimination of an unsaturated carbene centre and insertion into an *o*–C–H bond of the 3-phenyl group would form 7H-benzo[c]carbazole (17). It is not likely that we shall be able to confirm many of the features of this scheme, but experiments with ^{13}C-labelled or substituted precursors are planned. We have already established that the last step, (22)→(17), can occur, but these experiments will be reported with later evidence.
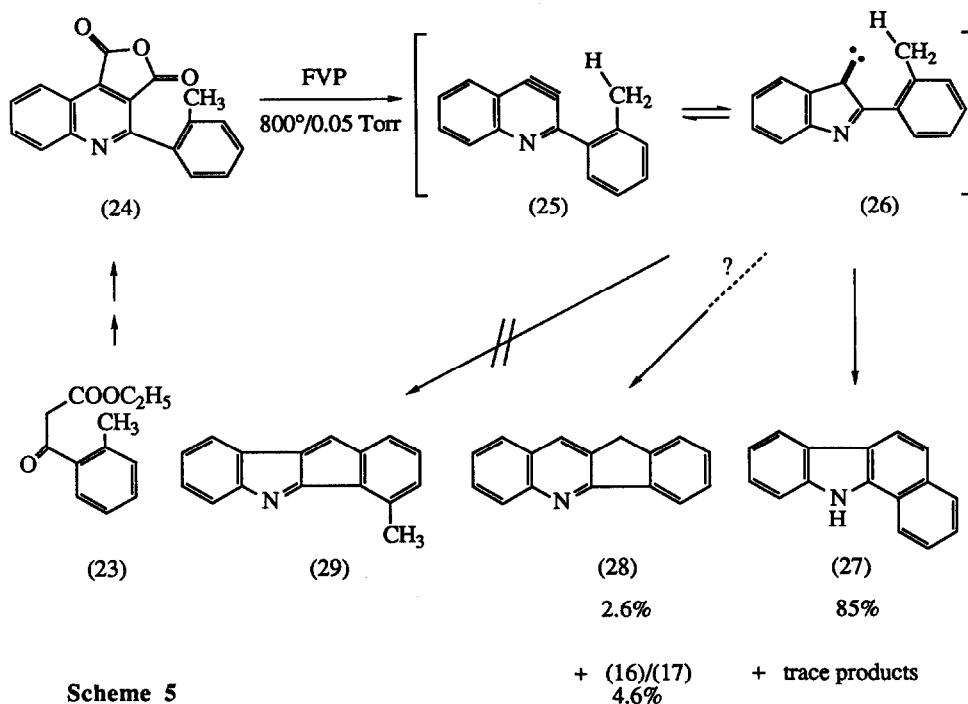
Scheme 4

FVP of 2-*o*-Tolylquinoline-3,4-dicarboxylic Anhydride (24)

The ketoester (23) required for the preparation of the title anhydride (24) was prepared by acylation of the dianion of monoethyl malonate with 2-methylbenzoyl chloride.[10] Pfitzinger condensation of this ketoester with isatin in 30% KOH, and cyclization of the resulting diacid with Ac$_2$O, gave the 2-*o*-tolyl anhydride (24) as colourless crystals, m.p. 176-177°. FVP of anhydride (24) at 800°/0.05 mm gave a dark green solid pyrolysate in 100% yield based on loss of CO$_2$ and CO only. The major product detected by [1]H n.m.r. was 11*H*-benzo[*a*]carbazole (27) in 85% yield (^{1}H NMR and GC), and this yellow crystalline product was readily isolated by flash chromatography on silica gel in 77% yield. The minor fraction of the pyrolysate appeared to be unstable to air, and an attempt was made to stabilise a second pyrolysate by reduction with LiAlH$_4$ in THF. The intention was to reduce 4-methylindeno[1,2-*b*]indole (29), if present, to the more stable 5,10-dihydro derivative. A GC and GCMS study of this pyrolysate showed that the major 11*H*-benzo[*a*]carbazole (85%) was accompanied by 5*H*-benzo[*b*]carbazole (16) and/or 7*H*-benzo[*c*]carbazole (17) (4%), and by 11*H*-indeno[1,2-*b*]quinoline (28) (2.6%). Five further trace components were observed by GCMS, with molecular ions at 217, 277, 233, 247 and 233, but none has been identified. The 5,10-dihydro derivative of (29), M=219, was not detected.

These pyrolytic results are summarised in Scheme 5. The major benzocarbazole (27) is clearly formed by insertion of the exocyclic carbene centre of (26) into the neighbouring methyl group, followed by *H*-migration. 11*H*-benzo[*a*]carbazole (27) was stable to re-pyrolysis at 800°, so that it is unlikely that the minor benzocarbazoles and 11*H*-indeno[1,2-*b*]quinoline (28) are secondary products of isomerization of (27).

Scheme 5

(24) → FVP 800°/0.05 Torr → (25) ⇌ (26)

(23) (29) (28) 2.6% (27) 85%

+ (16)/(17) 4.6% + trace products

The most direct route to 11H-indeno[1,2-b]quinoline (28) would involve H-migration from the methyl group of the aryne (25) to C-3 of the didehydroquinoline ring. This would generate the diradical (30) and cyclization to the same C-3 position could lead to the carbene (31), a plausible precursor of the indenoquinoline (28). We have recently used similar reasoning[11] to account for the formation of fluorene (49%) on pyrolysis of 3-(o-tolyl)phthalic anhydride at 860°. An alternative proposal for the formation of 11H-indeno[1,2-b]quinoline (28) starts with the initial product of carbene insertion into the methyl group in (26), and requires a dyotropic ring expansion of the resulting indolenine system (32, arrows) to form (28), in competition with H-migration leading to the major benzocarbazole (27). Ring expansion of 3-methyleneindolenine to quinoline has previously been proposed to account for the products of FVP of gramine at 820°, but the yield of quinoline was poor (13%).[12]

(30) (31) (32)
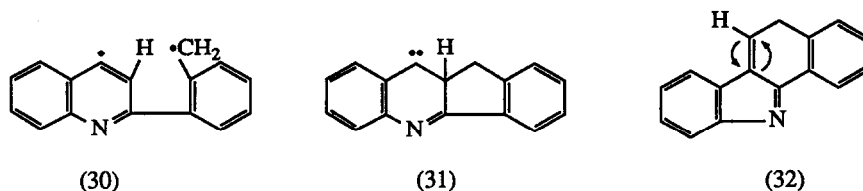
Conclusions

Although many uncertainties remain in the interpretation of minor pathways in the pyrolysis of the three quinoline-3,4-dicarboxylic anhydrides, the major products can be explained as products of interception of a ring-contracted exocyclic carbene by the neighbouring 2-aryl or 2-benzyl group. In the absence of contrary evidence

the exocyclic carbenes are assumed to be formed by thermal isomerization of the primary 2-substituted 3,4-didehydroquinoline intermediates.

Experimental

Microanalyses were carried out by the National Analytical Laboratories, Notting Hill, Vic. Infrared spectra (Perkin-Elmer FTIR 1600 instrument) refer to paraffin mulls of solids and thin films of liquids. ^{1}H (200MHz, 300MHz) and ^{13}C NMR (50.32MHz, 75.47MHz) spectra were recorded on Bruker AC-200 and AM-300 spectrometers, respectively, in CDCl$_3$ unless otherwise stated. Mass spectra were measured with a VG Trio-1 spectrometer at 70 eV. Analytical gas chromatography was carried out on a Varian 3700 gas chromatograph with flame ionization detection.

Silica gel for flash chromatography was Merck silicagel 60, particle size 0.040-0.063mm. Light petroleum refers to the fraction of b.p. 60-80°. Melting points were determined with a Reichert hot-stage melting point apparatus, and are uncorrected.

Samples of 11*H*-benzo[*a*]carbazole and 5*H*-benzo[*b*]carbazole were obtained from L. Light and Co. 7*H*-Benzo[*c*]carbazole [13] and 11*H*-indeno[1,2-*b*]quinoline [14] were prepared using literature methods.

The pyrolytic apparatus consisted of a horizontal silica tube (300 by 25mm i.d.) heated with an external electric furnace. The temperature was measured with a thermocouple placed on the external wall of the tube, and the pressure with a Dynavac TM 8 gauge mounted above the collecting cold finger, cooled with liquid nitrogen, at the exit end. The material to be pyrolysed was sublimed into the heated tube by warming with an air oven. Pyrolysis conditions [tube temperature (800°C), pressure (0.06mm), sublimation temperature (170°C), time to complete sublimation (30 min)], unless otherwise stated.

2-Phenylquinoline-3,4-dicarboxylic Acid

The acid was prepared by a modification of the method described by Engelhard.[5] Ethyl 3-oxo-3-phenylpropanoate (3.4 g, 17.7 mmol) was slowly added with stirring to aqueous KOH (50 ml, 10%) at 25°C. When the ester had dissolved, the solution was concentrated under vacuum to about 15 ml to give a slurry of potassium 3-oxo-3-phenylpropanoate. Isatin (2.6 g, 17.7 mmol) was dissolved in aqueous KOH (35 ml, 30%) and the solution was added to the slurry. The mixture was stirred at 25°C for 48h and the resulting solution was concentrated under vacuum until material began to precipitate. The mixture was then cooled in ice and the precipitated salt was collected. The salt was dissolved in the minimum amount of water, the solution was cooled and the acid was precipitated by dropwise addition of concentrated hydrochloric acid. The acid was collected, washed with ice-cold water and dried (2.3 g, 44%) , mp 193-196° (lit.[5] mp. 193-194°). IR (Nujol) ν_{max} 3521 b, 3280 b, 2564 b, 1690, 1644, 1600, 1582 cm^{-1}. ^{1}H NMR (D$_2$O)   δ 8.27-8.08 (m, 3H); 7.95 (apparent t, J = 7.5 Hz, 1H) ; 7.85-7.74, (m, 2H); 7.14-7.59 (m, 3H).   MS *m/z* 293 (M, 0.4%), 275 (39), 247(100), 219 (31), 203 (43).

2-Phenylquinoline-3,4-dicarboxylic Anhydride (4-Phenylfuro[3,4-*c*]quinoline-1,3-dione) (2)

A solution of 2-phenylquinoline-3,4-dicarboxylic acid (1.0 g, 3.6 mmol) in Ac$_2$O (20 ml) was refluxed for 3h. The excess reagent was evaporated under vacuum and the yellow crystalline residue was freed from traces of Ac$_2$O by standing over solid NaOH under vacuum. The resulting product was recrystallised from EtOAc to give the anhydride, as yellow crystals (0.67 g, 74%), mp 206-207° IR (Nujol) ν_{max} 1845 s, 1791 s, 1629 m, 1603 w cm^{-1}. ^{1}H NMR δ 8.83 (dd, J = 8.13, 1.90 Hz, H7); 8.13, dd, J = 8.13, 0.95 Hz, 1H); 8.08-7.90 (m, 3H); 7.86 (apparent t, J = 8.10 Hz, 1H); 7.62-7.54 (m, 3H). ^{13}C NMR δ 162.28, 161.31 (2×CO); 155.91, 151.91, 137.67, 135.50, 134.37, 130.71, 130.61, 130.42, 129.92 (2×C), 128.46 (2×C), 124.78, 9x arom. CH; 121.06, 120.42 (quat C). MS *m/z* 275 (M, 44%), 247 (100), 219 (31), 203 (30). Anal. calcd for C$_{17}$H$_9$NO$_3$: C, 74.5; H, 3.3; N, 5.1. Found: C, 74.5; H, 3.4; N, 4.8.

Indeno[1,2-*b*]indole (5)

FVP of 2-phenylquinoline-3,4-dicarboxylic anhydride (2) gave a red pyrolysate on the cold finger condenser and dark material at the exit from the furnace. The apparatus was filled with dry nitrogen and the pyrolysate was dissolved and manipulated under an inert atmosphere. The pyrolysate was more soluble in ether

than in $CHCl_3$ or CH_2Cl_2. Yields were determined after evaporation of the solvent and were generally in the range 30-40%. IR - The pyrolysate was deposited directly on to a NaCl plate cooled with liquid nitrogen and the spectrum measured under vacuum. v_{max} 3054 m, 1631 w, 1603 w, 1567 m, 1454 m, 1429 m, 1370 w, 1340 w, 1320 w, 1292 w, 1258 m, 1146 m, 1083 w, 1025 w, 935 w, 902 w, 863 w, 816 w, 784 w, 749 s, 732 w, 715 w cm^{-1}. The IR spectrum of the crystalline product obtained from CH_2Cl_2 when measured in Nujol had v_{max} 30050 m, 1626 w, 1605 w, 1565 m, 1338 w, 1320 w, 1292 w, 1258 m, 1144 m, 1083 w, 1022 w, 934 w, 904 w, 743 s cm^{-1}.UV - The pyrolysate was dissolved in ether and the spectrum measured. The concentration was determined by evaporation of an aliquot of solution and weighing the residue. λ_{max} 268 (4.73), 276 (4.87), 308 (3.45), 388 (3.60), 400 (3.59), 409 (3.73), 424 (3.46), 436 (3.58) nm (log e). ^{1}H NMR d 7.19-6.69 (m, arom 8H); 6.41 (s, 1H). ^{13}C NMR δ 177.41(?), 166.13 (?), 151.67, 143.32, 130.01 (only 5 quat C detected); 132.00, 131.95, 130.01, 128.94, 126.86, 124.62, 123.41, 123.19, 122.18 (9x arom CH). MS - The CH_2Cl_2 solution was immediately evaporated under vacuum and the crystalline residue introduced into the spectrometer. m/z 203 (M, 100%), 176 (7), 102 (12), 88 (9), 75 (7). HRMS (EI) exact mass calc for $C_{15}H_9N$, 203.073; found 203.073 ± 0.002.

5,10-Dihydroindeno[1,2-b]indole (6)

(i) This compound was prepared by the method of Seka and Kellermann[7] from 1-indanone, phenylhydrazine and aqueous methanolic hydrochloric acid and recrystallised from EtOH to give nearly colourless plates, mp 235° (dec.) (lit.[7] mp 238-248° dec.). IR (Nujol) v_{max} 3407 s (NH), 1609 w, 1524 w, 1500 m, 1406 m, 1306 m, 1248 m , 1091 w, 1012 w, 761 m, 740 s, 721 m cm^{-1}. UV (CHCl$_3$) λ_{max} 323 (4.74) nm (log ε). ^{1}H NMR (DMSO-d$_6$) δ 11.61(s,NH); 7.60 (d, J = 7.46 Hz, 1H); 7.55 (apparent t, J = 7.34 Hz, 2H); 7.46 (d, J = 7.80 Hz, 1H); 7.35 (d, J = 7.36 Hz, 1H); 7.20 (apparent t, J = 7.34 Hz, 1H); 7.13-7.02 (m, 2H); 3.68 (s, CH$_2$). ^{13}C NMR (DMSO-d$_6$) δ 147.41, 143.57, 140.70, 135.09, 124.11, 119.84 (6x quat C); 126.61, 125.43, 124.57, 120.97, 119.84, 119.27, 118.58, 117.71, 112.39 (8x arom CH); 29.81 (CH$_2$). MS m/z 205 (M, 100%), 204 (78), 203 (19), 176 (8), 103 (19), 102 (24).

(ii) The anhydride (2) (140 mg) was pyrolysed (800°, 0.06 mm, 175°, 80 min,). The apparatus was allowed to come to 25°C under vacuum and it was then filled with hydrogen. The pyrolysate was washed from the condenser with ether directly into a flask containing Pd/C catalyst (15 mg, 10%) and a spin bar. The suspension was stirred for 10 h under hydrogen. The resulting mixture was filtered, the solvent evaporated and the residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum , 1:4) to give a crystalline product (10 mg, 10%) which was recrystallised from EtOH, mp 235° dec.. The compound was identified as 5,10-dihydroindeno[1,2-b]indole by means of IR, ^{1}H and ^{13}C NMR and MS.

(iii) The anhydride (2) (136 mg) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was washed from the cold finger condenser with ether (50 ml) into a slurry of LiAlH$_4$ (0.2 g) in ether (5 ml). The mixture went colourless almost immediately. It was stirred for 1 h and then water was added dropwise until gas evolution ceased. The mixture was filtered through celite and the filtrate evaporated to leave a colourless solid. The product was flash chromatographed (SiO$_2$: EtOAc/light petroleum, 1:6) to give 5,10-dihydroindeno[1,2-b]indole as colourless plates (16 mg. 18%), mp 235° dec.. The compound was identified as (6) by means of IR, MS and ^{1}H NMR. ^{13}C NMR δ 147.78, 143.28, 140.80, 135.00, 124.75, 121.80 (6x quat C); 126.51, 125.46, 124.75, 121.69, 120.21, 118.94, 117.25, 112.01 (8x arom CH); 30.35 (CH$_2$).

10-(Diethylamino)-5,10-dihydroindeno[1,2-b]indole (7)

The anhydride (2) (128mg, 0.46mmol) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was washed down with ether into a flask containing Et$_2$NH (0.5ml). The resulting colourless solution was evaporated under vacuum and the residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:3) to give 7 as a light tan solid (37mg, 29%). It was recrystallised from light petroleum to give light tan needles, m.p. 125-126° (lit.[6a] mp 126-126.5°). IR (Nujol) v_{max} 3402 (NH), 1302 cm^{-1}. ^{1}H NMR δ 8.34 (s, br, NH); 7.68-7.60 (m, 2H); 7.46-7.40 (m, 1H); 7.40-7.27 (m, 2H); 7.24-7.13 (m, 3H); 4.89 (s, 1H) (s, 1H); 2.57 (q, J = 7.0 Hz, 2×CH$_2$); 1.12 (t, J = 7.0 Hz, 2×CH$_3$). ^{13}C NMR δ 151.19, 143.55, 140.58, 134.05, 125.30, 123.29 (6×quat C); 127.32, 125.56, 125.53, 121.66, 120.63, 120.48, 116.93, 112.03, 112.03 (8×arom CH); 62.98, (CH); 46.06 (2×CH$_2$); 14.67 (2×CH$_3$). MS m/z 276 (M, 30%), 247 (18), 205 (17), 204 (84), 203 (100), 202 (14), 176 (20), 72 (16), 58 (24).

5,10-Dihydro-10-phenylindeno(1,2-*b*)indole (8)

(i) 3-Phenylindan-1-one[15] was converted into the phenylhydrazone which was heated in polyphosphoric acid (100°, 30 min) to give the indole 8. This was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:9) to give a colourless solid (48% yield) which on recrystallization from CCl$_4$ gave colourless crystals, m.p. 170-172°, decomposing to a brown melt. A sublimed sample (170°/0.1mm) melted with decomposition similarly at 177-178° (Eisch and Abraham[8] gave m.p. 228-230°). IR (Nujol) v_{max} 3406 (NH), 744, 700 cm^{-1}. ^{1}H NMR δ 8.37 (s, br, NH); 7.50-7.02 (m, arom. 13H); 4.99 (s, CH). ^{13}C NMR δ 152.65, 142.76, 140.71, 140.50, 134.13, 125.76, 124.30 (7×quat C); 128.60 (2×C), 127.90 (2×C), 126.94, 126.71, 125.44, 125.38, 121.86, 120.33, 118.95, 117.35, 112.03 (13×arom. CH); 48.70 (CH). MS *m/z* 281 (M, 100), 280 (89), 278 (17), 204 (41), 176 (15), 141 (14), 139 (26). Anal. Calcd C$_{21}$H$_{15}$N: C, 89.65; H, 5.4; N, 5.0. Found: C, 89.4; H, 5.6; N, 5.3.

(ii) The anhydride (2) (136mg, 0.5mmol) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was dissolved in anhydrous ether. Phenyllithium was prepared by addition of bromobenzene (1ml) to lithium (0.14g) in ether (5ml) and a portion of this solution (1ml, 2mmol) was placed in a flask under nitrogen. The ethereal solution of the pyrolysate was added slowly to the phenyllithium at 25°C with stirring and the mixture was stirred for 1h. Water was then added dropwise to the reaction mixture, the ether layer was separated, washed with water, dried (Na$_2$SO$_4$) and evaporated under vacuum. The residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:6) to give the phenyl derivative (8) as a yellow solid. The compound was recrystallised from CCl$_4$ and obtained as colourless crystals (33mg, 23%), m.p. 176-177°, decomposing to a brown melt. The compound was shown to be identical with that described above by means of IR, ^{1}H NMR, ^{13}C NMR and MS.

5,10-Dihydro-10-methoxyindeno(1,2-*b*)indole (9)

The anhydride (2) (136mg, 0.5mmol) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was dissolved in anhydrous ether and added to NaOMe in MeOH (0.1g sodium dissolved in MeOH, 5ml). The red colour of the pyrolysate disappeared immediately. Dilute hydrochloric acid was added and the ethereal layer was separated, washed with water, dried (Na$_2$SO$_4$) and the ether evaporated. The residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:6) to give 9 as an oil which solidified slowly on standing (20mg, 18%), m.p. 93-95°. The compound decomposed on attempted sublimation or recrystallisation. IR (Nujol) v_{max} 3400 br (NH), 3055, 1710, 1610, 1265, 1103, 1069, 742, 703 cm^{-1}. ^{1}H NMR δ 8.41 (s, br, NH); 7.74-7.15 (m, arom 8H); 5.55 (s, 1H); 3.28 (s, OCH$_3$). ^{13}C NMR δ 148.30, 144.11, 140.58, 134.36, 125.03, 120.94 (6×quat C); 128.44, 126.22, 125.86, 122.06, 120.97, 119.40, 117.39, 112.14 (8×arom CH); 77.29 (CH); 55.54 (OCH$_3$). MS *m/z* 235 (M, 54%), 220 (50), 219 (17), 204 (55), 203 (100), 202 (17), 176 (13), 103 (12), 101 (13), 88 (19). HRMS (EI) exact mass calcd for C$_{16}$H$_{13}$ NO, 235.100; Found 235.100 ±0.002.

5,10-Dihydro-10-methylindeno(1,2-*b*)indole (11)

The anhydride (2) (114mg, 0.4mmol) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was washed down with anhydrous ether (50ml) directly into ethereal MeMgI (2ml, 8mmol). The mixture was allowed to stand for 1h at 25°C and was then poured into ice and sulfuric acid (2M). The ether layer was separated, washed with aqeous NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and the ether evaporated under vacuum. The residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:6) to yield 10 as a pale yellow solid (22mg, 24%), m.p. 159-161°. The compound decomposed on sublimation or recrystallisation. IR (Nujol) v_{max} 3394 (NH), 1609w, 1310, 1247, 741 cm^{-1}. ^{1}H NMR δ 8.26 (s, br, NH); 7.69-7.64 (m, 1H); 7.53-7.49 (m, 1H); 7.46-7.41 (m, 2H); 7.35-7.28 (m, 1H); 7.27-7.13 (m, 3H); 3.93 (q, *J* = 7.4 Hz, 1H); 1.60 (d, *J* = 7.4 Hz, CH$_3$). ^{13}C NMR δ 153.82, 140.67, 134.13, 131.39, 117.13, (6×quat C); 126.61, 124.99, 124.17, 121.62, 120.17, 118.68, 117.27, 112.08 (8×arom CH); 37.41 (1×CH); 17.55 (1×CH$_3$). MS *m/z* 219 (M, 50%), 218 (17), 216 (18), 205 (18), 204 (100), 203 (17), 110 (10), 109 (17), 102 (19). HRMS (EF) exact mass calcd for C$_{16}$H$_{13}$N, 219.105; found 219.105±0.002.

Dimethyl 2-(5',10'-dihydroindeno(1,2-*b*)indol-10'-yl)propanedioate (11)

The anhydride (2) (120mg, 0.44mmol) was pyrolysed and under an atmosphere of nitrogen the

pyrolysate was washed down with anhydrous ether into a suspension of sodium dimethyl malonate in ether (prepared from dimethyl malonate (0.1ml), NaOH (0.1g) and ether (5ml)). The colour of the pyrolysate disappeared as the mixture was stirred. Water was added and the ether layer was separated, washed with dilute hydrochloric acid and water, dried (Na$_2$SO$_4$) and evaporated under vacuum. The residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:3) to give the *ester* (11) as a colourless oil which crystallised on standing (25mg, 17%), m.p. 147-148°. The compound decomposed on sublimation or recrystallisation. IR (Nujol) v_{max} 3412 (NH), 1748, 1718, 1611, 1260, 1176, 1135, 1020, 750, 741 cm^{-1}. ^{1}H NMR δ 8.40 (s, br, NH); 7.62-7.58 (m, 1H); 7.45-7.10 (m, 7H); 4.71 (d, J = 7.93 Hz, H10'); 3.77 (s, OCH$_3$); 3.70 (d, J = 7.93 Hz, H2); 3.64 (s, OCH$_3$). ^{13}C NMR δ 168.98, 168.91 (2×CO); 148.66, 143.11, 140.63, 134.38, 124.29 (only 5×quat C detected); 127.63, 125.46, 124. 91, 121.93, 120.50, 119.67, 117.61, 112.03 (8×arom CH); 54.90 (CH); 52.67, 52.60 (2×OCH$_3$); 42.27 (CH). MS *m/z* 335 (M, 23%), 275 (10), 244 (7), 217 (11), 216 (14), 205 (14), 204 (14), 204 (100), 176 (8). HRMS (EI) exact mass calc for C$_{20}$H$_{17}$NO$_4$, 335.116; found, 335.114 ± 0.003.

5,10-Dihydro-10-(1'-methyl-1'-nitroethyl)-indeno[1,2-*b*]indole (12)

The anhydride, (2) (119mg, 0.44mmol) was pyrolysed and under an atmosphere of nitrogen the pyrolysate was washed down with anhydrous ether into a suspension of the sodium salt of 2-nitropropane [prepared by addition of 2-nitropropane (0.2ml) to NaH (0.1 g) in anhydrous ether (1 ml)]. The mixture was stirred at 40° for 30 min in which time the red colour disappeared. Water was added, the ether layer was separated, washed with dilute hydrochloric acid and water, dried (Na$_2$SO$_4$) and evaporated. The residue was flash chromatographed (SiO$_2$; EtOAc/light petroleum, 1:5) to give the product (28mg, 22%). The compound was recrystallised from CH$_2$Cl$_2$/light petroleum (*ca.* 1:9) and sublimed (155°/0.05mm) to give 12 as yellow crystals, mp 163-165°. IR (Nujol) v_{max} 3405 (NH), 1616w cm^{-1}. ^{1}H NMR δ 8.41 (s, b, NH); 7.61-7.56 (m, 1H); 7.46-7.40 (m, 2H); 7.38-7.31 (m, 1H); 7.25-7.13 (m, 4H); 4.82 (s, H10); 1.80 (s, CH$_3$); 1.30 (s, CH$_3$). ^{13}C NMR δ 146.62, 144.06, 140.69, 134.82, 124.58, 120.34, 90.68 (7×quat C); 127.97, 125.85, 125.18, 122.18, 120.96, 119.74, 117.69, 112.23 (8×arom CH); 51.60 (1×CH); 26.14, 21.31 (2×CH$_3$). MS *m/z* 292 (M, 27%), 246 (40, 245 (49), 231 (55), 230 (39), 217 (21), 205 (19), 204 (100), 203 (59). Anal. calcd for C$_{18}$H$_{16}$N$_2$O$_2$: C, 73.95; H, 5.5; N, 9.6. Found: C, 73.8; H, 5.9; N, 9.9.

2-Benzylquinoline-3,4-dicarboxylic anhydride (13)

Methyl 4-phenyl-3-oxobutanoate[9] (0.81g, 5mmol) was added slowly to aqueous KOH (10%, 15ml) at 20°. The ester dissolved during 1h and the solution was concentrated to about 5ml. To this was added a solution of isatin (0.74g, 5mmol) in aqueous KOH (30%, 10ml) and the mixture was stirred for 6h and then allowed to stand for 3 days. The resulting solution was concentrated under vacuum until a precipitate formed and the mixture was then cooled in ice. The yellow solution was decanted from the brown gummy precipitate of potassium salt, which was dissolved in a minimum of water and the solution acidified with conc. hydrochloric acid. The precipitated acid was collected, redissolved in aqueous NaHCO$_3$, filtered and reprecipitated with conc. hydrochloric acid to give 2-benzylquinoline 3,4-dicarboxylic acid, as a brown solid (0.98g, 64%), m.p. 170-175°. IR (Nujol) v_{max} 2526 (OH), 1737 (C=O), 1654w, 1613, 1583 cm^{-1}. ^{1}H NMR (CDCl$_3$/DMSO-d$_6$) δ 8.13-8.07 (m, H5, H8); 7.83-7.74 [m, H7 (6)]; 7.64-7.55 [m, H6 (7)]; 7.35-7.10 (m, aromatic); 4.63 (s, CH$_2$). MS *m/z* 289 (M-18, 93%), 261 (38), 218 (19), 217 (100), 216 (65), 215 (27), 214 (20), 204 (15), 189 (26), 108 (35). The diacid (0.5g, 1.6mmol) and Ac$_2$O (5ml) were heated at 100° for 1.5h. The mixture was cooled and a trace of solid material was removed by filtration and discarded. The filtrate was evaporated under vacuum and the residue was recrystallised from EtOAc/light petroleum (1:2) to yield 13, as yellow crystals (0.15g, 32%), mp 144-145°. The anhydride was further purified by sublimation (130°/0.001mm). IR (Nujol) v_{max} 1853m, 1793s (anhydride), 1628, 1601, 1246, 1212, 1178, 1135, 914, 779, 703cm^{-1}. ^{1}H NMR δ 8.72 (dq, J = 8.33Hz, H5); 8.30 (dq, J = 8.52Hz, H8); 8.02 (ddd, J = 8.64, 6.92, 1.50 Hz, H7; 7.83 (ddd, J = 8.25, 7.04, 1.27 Hz, H6); 7.48 (dd, J = 8.04, 1.51 Hz, 2H); 7.33-7.16 (m, 3H); 4.74 (s, CH$_2$). ^{13}C NMR δ 162.12, 162.00 (2× C=O); 157.88, 152.02, 137.16, 136.87, 121.88, 120.51 (6×quat C); 134.02, 130.21, 130.15, 129.34 (2×C), 128.58 (2×C), 126.90, 124.70 (9×arom. CH); 41.08 (CH$_2$). MS *m/z* 289 (M, 100%), 261 (38), 218 (17), 217 (95), 216 (60), 215 (26), 214 (19), 189 (21), 108 (20). Anal. calcd for C$_{18}$H$_{11}$NO$_3$: C, 74.7; H, 3.8; N, 4.8. Found: C, 74.6; H, 3.7; N, 4.8.

Pyrolysis of 2-Benzylquinoline-3,4-dicarboxylic Anhydride (13)

Pyrolysis (800°, 0.03mm, 120°, 1h) of anhydride (13) (50mg, 0.17mmol) gave a pyrolysate which

condensed principally at the inlet to the trap. This was washed down with CH_2Cl_2 and then with acetone to give a red solution which was evaporated to give a red solid (39mg). The mixture was radial chromatographed (SiO_2; 2mm plate; EtOAc/light petroleum, 1:9) to give yellow crystalline compounds, 7H-benzo[c]carbazole, m.p. 122-127° (lit [16] m.p. 137-138°) and 5H-benzo[b]carbazole, m.p. >300° (lit.[17] m.p. 332°). The products were present in a ratio of approx. 2:1 and they were identified with authentic samples by ^{1}H NMR, HPLC (CH_3CN/H_2O 80%) and GCMS.

Ethyl 3-(2'-methylphenyl)-3-oxobutanoate (23)

Under an atmosphere of nitrogen monoethyl malonate[18] (5.5g, 42mmol) was dissolved in anhydrous THF (100ml) and 2,2'-bipyridyl (10mg) was added as an indicator. The mixture was stirred and cooled to -78° and buLi in hexane (2.5M, 34ml, 84mmol) was added slowly (syringe) while the temperature was allowed to rise to -5° near the end of the addition (30 min.). After the pink colour had persisted at -5° for ca. 3 min., the heterogeneous mixture was cooled to -78° and 2-methylbenzoyl chloride (3.5g, 23mmol) was added dropwise over 5 min. The mixture was stirred, the cooling bath was removed and over a period of 1h the temperature rose to 20°. The reaction mixture was poured into a mixture of ether (200ml) and hydrochloric acid (1M, 120ml). The ether layer was separated, washed twice with aqueous $NaHCO_3$ and with water, dried (Na_2SO_4) and the ether evaporated under vacuum to give the ketoester, as a yellow oil. The compound was distilled (bulb to bulb; oven temp. 150°/2mm) to give 23, as a colourless oil (3.4g, 72%). IR v_{max} 1743, 1688, 1627, 1319, 1260, 1192, 1150, 1033, 758 cm^{-1}. ^{1}H NMR δ 7.69-7.63 (m, 1H); 7.45-7.19 (m, 3H); 5.28 (s, enol=CH–, 0.25H); 4.26 (q, J = 7.1Hz, enol–OCH_2, 0.5H); 4.19 (q, J = 7.1Hz, keto–OCH_2, 1.5H); 3.95 (s, keto CH_2, 1.5H); 2.55 (s, $ArCH_3$, 2.25H); 2.46 (s, $ArCH_3$, 0.75H); 1.33 (t, J = 7.1 Hz, enol–OCH_2CH_3, 0.75H); 1.24 (t, J = 7.1 Hz, keto–OCH_2CH_3, 2.25H); OH not observed. ^{13}C NMR δ 195.58, 174.90 (2×CO); 167.59, 139.38, 136.55, 136.24, (4×quat C); 132.25, 132.11, 129.14, 125.79 (4×arom CH, keto); 131.00, 130.02, 128.41, 125.74 (4×arom. CH, enol); 91.65 (CH, enol); 61.35 (OCH_2, keto); 60.28 (OCH_2, enol); 48.27 (?); 21.51 ($ArCH_3$, keto); 20.51 ($ArCH_3$, enol); 14.29 (OCH_2CH_3, enol); 14.05 (OCH_2CH_3, keto). MS m/z 206 (M, 14%), 160 (7), 119 (100), 118 (36), 91 (51). Anal. calcd $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 69.8; H, 6.5.

2-(2'-Methylphenyl)-quinoline-3,4-dicarboxylic Anhydride (4-(2'methylphenyl)-furo[3,4-c]quinoline-1,3-dione) (24)

The ketoester (23) (3.35g, 16.3mmol) was added slowly to aqueous KOH (10%, 50ml). After the ester had dissolved (1.5h) the solution was concentrated to ca. 15ml. Isatin (2.39g, 1.3mmol) was dissolved in aqueous KOH (30%, 32ml) and the two solutions were mixed and allowed to stand at 25°C for 19 days. The resulting orange solution was extracted twice with ether to remove any neutral material and the aqueous phase was cooled and acidified to yield a yellow solid. This product was collected and redissolved in saturated aqueous $NaHCO_3$. The solution was filtered and acidified with concentrated hydrochloric acid to give the diacid as a pale yellow solid (3.64g, 73%), mp 185-188°. IR (Nujol) max 2502 (br, OH), 1732 (CO), 1644, 1614, 1585 cm^{-1}. ^{1}H NMR ($CDCl_3/DMSO-d_6$) δ 8.22 [d, J = 7.57Hz, H5(8)]; 8.13 [d, J = 7.84Mz, H8(5)]; 7.83 [apparent t, J = 7.70 Hz, H7(6)]; 7.67 [apparent t, J = 7.64Hz, H6(7)]; 7.36-7.18 (m, 4H, arom); 2.25 (s, CH_3). The diacid (0.44g, 1.4mmol) in Ac_2O (5ml) was refluxed for 2h. The mixture was concentrated under vacuum to half the volume and cooled to 0° when the product crystallised. The crystals were collected and washed with cold EtOAc. The filtrate and washings were evaporated and the residue was sublimed (150°/0.1mm) to yield additional anhydride (total yield 0.13g, 70%). The anhydride was resublimed to give colourless crystals, m.p. 176-177°. IR v_{max} 1852, 1795 cm^{-1}. ^{1}H NMR δ 8.86 (d, J = 8.4Hz, H5); 8.36 (d, J = 8.5 Hz, H8); 8.07 [apparent t, J = 7.8 Hz, H7 (6)]; 7.92 [apparent t, J = 7.3Hz, H6(7)]; 7.50-7.36 (m, 3H, arom); 2.28 (s, CH_3). ^{13}C NMR δ 161.25, 160.87 (2×CO); 156.69, 151.77, 136.78, 136.35, 135.28, 134.37, 120.53 (7×quat C); 134.33, 130.78, 130.72, 130.72, 130.44, 129.95, 129.66, 125.88, 124.81 (8×arom C); 19.78 (CH_3). MS m/z 289 (M, 1.8%), 245 (3.0), 233 (2.6), 217 (100), 204 (12). Anal. calcd $C_{18}H_{11}NO_3$: C, 74.73; H, 3.83; N, 4.84. Found: C, 74.7; H, 3.9; N, 4.8.

Pyrolysis of 2(2'-Methylphenyl)-quinoline-3,4-dicarboxylic anhydride (24)

(i) The anhydride (24) (100mg, 0.35mmol) was pyrolysed (800°, 0.05mm, 150°, 1.5h). The pyrolysate condensed as a yellow-green deposit at the trap inlet. It was dissolved in CH_2Cl_2 and evaporation of the solvent left a dark green solid (75mg, 100% based on $C_{16}H_{10}N$). The ^{1}H NMR spectrum showed the product to be principally 11H-benzo[a]carbazole (27), which was flash chromatographed (SiO_2; EtOAc/light petroleum, 1:9;

followed by 1:4) and the 11*H*-benzo[*a*]carbazole was isolated as yellow crystals (58mg, 77%), mp 190-238°. The product was shown to be identical with an authentic sample by means of ^{1}H NMR, melting behaviour, GC and GCMS.

(ii) The anhydride (24) (95mg) was pyrolysed under the same conditions and, under an atmosphere of nitrogen, the pyrolysate was washed down with anhydrous THF (15ml) into LiAlH$_4$ (0.16g). The green mixture was stirred at 20° for 2h. Water (4 drops) was added, the mixture was filtered through celite and the solvent was evaporated. The ^{1}H NMR spectrum and GC showed the major product to be 11*H*-benzo[*a*]carbazole (27) (80-85% yield). GCMS (silica capillary, 25m, BP5, 150° 1min., 150-280° at 10°/min.) t$_r$ 11.454 min. (*m/z* 217) (11*H*-indeno[1,2-*b*]quinoline (28)), 12.081 (217), 12.241 (277), 12.881 (233), 13.428 (217) (11*H*-benzo[*a*]carbazole (27)), 14.147 (217) (5*H*-benzo[b]carbazole and/or 7*H*-benzo[*c*]carbazole (16/17)), 15.307 (247), 15.521 (233). Relative yields were determined by GC (180×6.3mm, glass column, 10% SE 30, 150° 1min., 150-280° at 10°/min) 11*H*-indeno[1.2-*b*]quinoline (28) 2.6%; 11*H*-benzo[*a*]carbazole (27), 85%; 5*H*-benzo[*b*]carbazole (16) and or 5*H*-benzo[*c*]carbazole (17), 4%.

Pyrolysis of 11*H*-benzo[*a*]carbazole, 5*H*-benzo[*b*]carbazole and 7*H*-benzo[*c*]carbazole

(a)   11*H*-Benzo[*a*]carbazole was recovered unchanged after FVP at 800°/0.02mm.

(b)   On FVP of 5*H*-benzo[*b*]carbazole at 800°/0.02mm, half of the material was recovered unchanged and the pyrolytic products did not contain either the 11*H*-benzo[*a*]carbazole or the 7*H*-benzo[*c*]carbazole.

(c)   7*H*-Benzo[*c*]carbazole was recovered unchanged after FVP at 800°/0.02mm.

Acknowledgement

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