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INDOLE-2, 3-QUINODIMETHANES

SYNTHESIS OF INDOLOCARBAZOLES FOR THE SYNTHESIS OF THE FUSED DIMERIC INDOLE ALKALOID STAUROSPORINONE

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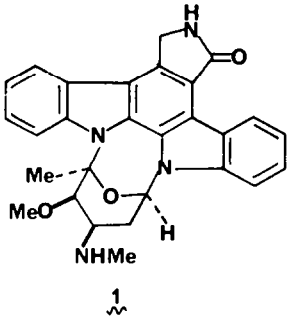
Abstract—N-[(4-Methoxyphenyl)sulfonyl]-3-ethyl-2-formylindole, made by direct electrophilic formylation of N-[(4-methoxylphenyl)sulfonyl]-3-ethylindole using α, α-dichloromethylmethylether/$TiCl_4$, was converted into the imine **23** by treatment with 2-aminostyrene. The imine **23**, on treatment with methylchloroformate gave the hexahydroindolocarbazole **24**, which was dehydrogenated (DDQ) to give the completely aromatic system **25**. Other examples of this type of methodology for the synthesis of both indolocarbazoles and pyrrolocarbazoles are described.

INTRODUCTION

In 1979, the structure of the unusual fused dimeric indole alkaloid staurosporine **1** was reported.[1] The only analogous structure is one of the trimeric products formed by treatment of indole with acid.[2] Staurosporine exhibits strong hypotensive activity, and antimicrobial activity against fungi and yeast.

The synthesis of the aglycone staurosporinone **2**, offers us an opportunity to examine the intramolecular trapping of an indole-2, 3-quinodimethane intermediate, where the dienophile is attached to the 2-position of an indole rather than the 3-position. Previously we have used N[1]-4-methoxyphenylsulfonyl-2-methyl-3-formylindole **3** as a precursor to



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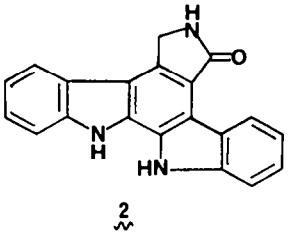

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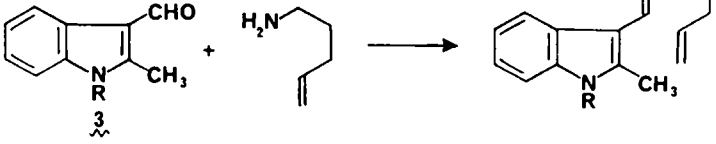

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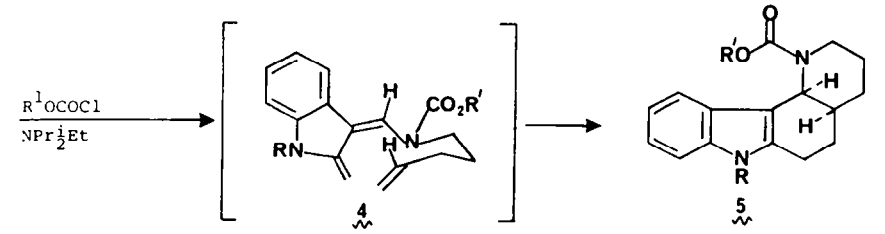


4 5

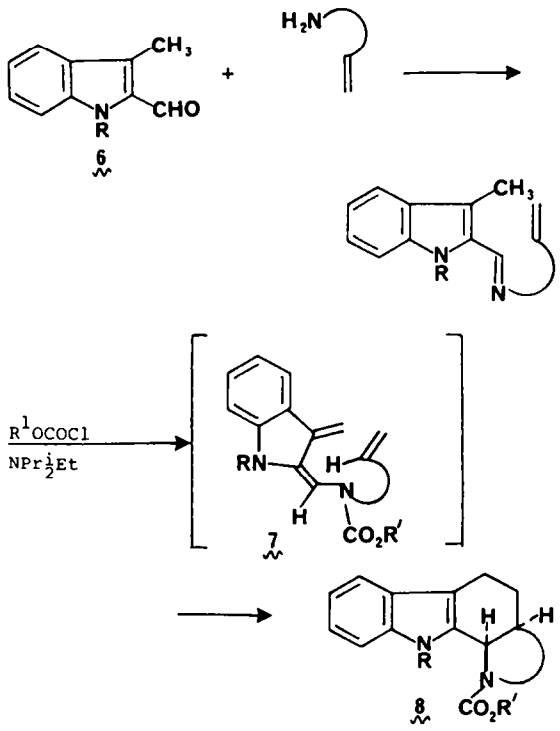
R = 4-$MeOC_6H_4SO_2$-, throughout)

Scheme 1.

tetracyclic pyridocarbazoles **5**, *via* an indole-2, 3-quinodimethane intermediate **4** (Scheme 1).[3] This type of strategy has lead to short convergent syntheses of aspidospermidine,[4] kopsanone and 10, 22-dioxokopsane.[5]

To investigate the regiochemical reversal of Scheme 1, namely Scheme 2, necessitates the synthesis of 3-methyl-2-formylindole derivatives **6**. Surveillance of the literature revealed that while 2-formyl-3-methylindole is a known compound, it is not readily accessible.[6] Here we describe the experimental implementation of Scheme 2, the synthesis of 3-alkyl-2-formylindole derivatives, and the synthesis of indolocarbazoles **20** and **25**.

Comparison of the reactivity of the intermediate indole-2, 3-quinodimethane **4**, with **7**, would predict that the diene **7** is more electron deficient than **4**, and consequently should be considerably more reactive towards electron rich alkenes. The stereochemical outcome of an *exo*-type transition state, for the geometry shown in **7**, predicts that the tetracyclic product **8**, will have the newly formed ring fusion *cis*.[3] The *E*-relationship of the two nitrogen substituents in **7** is favored over a *Z*-configuration, since the latter produces a severe steric compression between them. Both the above predictions are corroborated by the experimental results.



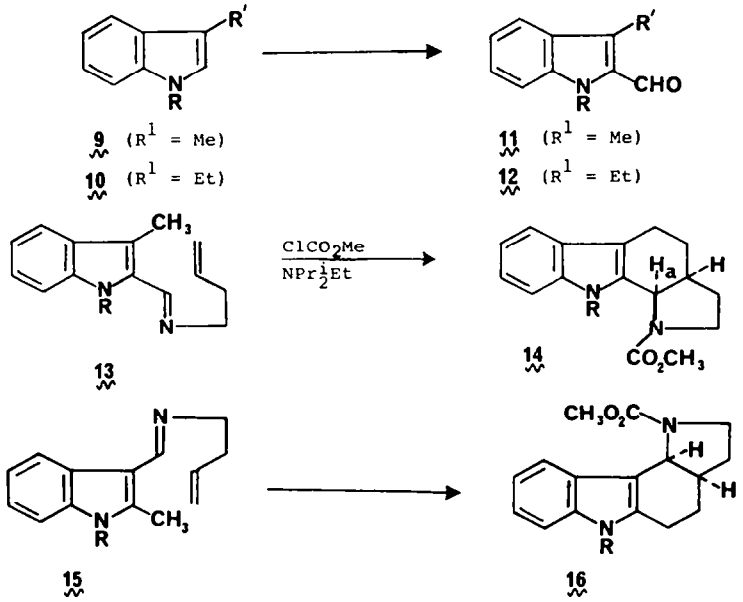
Scheme 2.

RESULTS

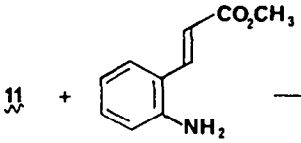
N-Arylsulfonylindoles[7] were originally intended to direct metallation (usually lithiation), into the vacant 2-position of the indole ring, which on subsequent quenching with an electrophile provides a very useful route to 2-substituted indole derivatives. While this works well for a wide range of electrophiles, the results with dimethylformamide, N-methylformanilide and N-formylmorpholine, were not particularly encouraging for the introduction of a 2-formyl group. Since, as we have already alluded to, the literature method for the synthesis of 3-methyl-2-formylindole is not particularly convenient,[6] we decided to examine the electrophilic formylation of N-4-methoxysulfonyl-3-methylindole **9**.

Treatment of **9** with $Cl_2CHOMe/CH_2Cl_2/SnCl_4$[8] at $-25°$, gave after work-up (1N HCl) the required 2-formyl derivative **11** (66%). Similarly, the 3-ethylindole **10**, on treatment with $Cl_2CHOMe/CH_2Cl_2/TiCl_4$ gave the required formyl derivative **12** (64%).

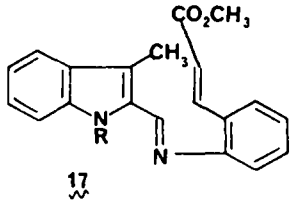
The 2-formyl-3-methylindole **11** was treated with but-3-enylamine,[9] in the presence of 4A molecular sieves, to give the imine **13**. When the imine **13** was



exposed to methylchloroformate (3 eq.) in the presence of NPr^i_2Et at 135° (PhCl solv.) for 1 h the *cis*-fused tetracyclic carbamate **14** was isolated in 84% yield (Ha, 5.41 d, J = 4 Hz). Similarly treatment of the imine **15** with methyl chloroformate (3.3 eq.) in the presence of NPr^i_2Et at 135° (PhCl solv.) for 5 hr gave the isomeric tetracycle **16** (40%). The conditions and yield of **14** should be contrasted with **16**; and is in agreement with the predictions made earlier.



11



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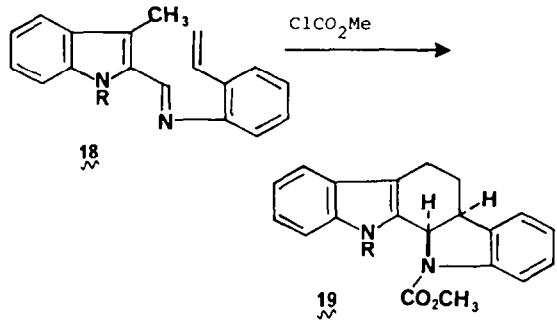
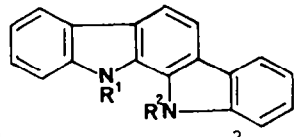
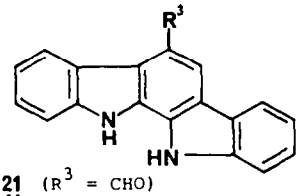
Condensation of **11** with (*E*)-methyl-2-aminocinnamate[10] gave the stable, crystalline imine **17** (99%). Not too surprisingly, when **17** was exposed to the same conditions that converted **13** into **14**, no reaction was observed. Even heating **17** with ethylchloroformate (5 eq.) at 180°C did not cause any change. The imine nitrogen atom in **17** is substantially less basic than in **13**, and therefore not so readily acetylated; furthermore the dienophilic component of **17**, being electron deficient, would not react readily with an electron deficient diene (see **7**). We were unable to reduce the ester group in **17** or precursors to **17**, and consequently decided to place the one carbon substituent in the preformed indole component. It should be noted that staurosporinone **2** is symmetrical with respect to substitution, although not oxidation level. Before proceeding to substituted systems, we decided to test whether or not a simple *ortho*-vinylarylimine would undergo intramolecular[2 + 4] cycloaddition to an indole-2, 3-quinodimethane. Treatment of **11** with 2-aminostyrene[11] (4 Å molecular sieves) gave the stable crystalline imine **18**, m.p. 162–163°C. When this imine was exposed to methylchloroformate (5 eq.) in chlorobenzene at 110° for 2 hr the pentacyclic carbamate **19** was formed in 89% yield. In the ^{1}H NMR spectrum Ha appears as a doublet δ6.15 (J = 7 Hz), substantiating the assigned *cis*- ring fusion. Dehydrogenation of **19** (DDQ/Toluene/110°) gave the parent indolocarbazole **20** (64%), m.p. 217–218°.[12] λ_{max}^{EtOH} 232, 288, 307 and 340 nm (ϵ, 28,990, 13670, 13610, and 15980). An attempt to formylate **20**, or the free diamine **20**, ($R^1 = R^2 = H$) were unsuccessful. A suitable precursor to the aldehyde **21** was thought to be the corresponding methyl compound **22**. The 3-ethyl-2-formylindole **12** condensed with 2-aminostyrene to give the imine **23**. Treatment of **23** with MeOCOCl (5.5 eq.)/PhCl/135°/6 h gave the pentacyclic carbamate **24** (81%). Dehydrogenation (DDQ) of **24** gave **25** (64%), λ_{max}^{EtOH} 246, 274, 284, 306, 318 and 340 nm (ϵ 26450, 13670, 12840, 14390, 13460 and 3400). All attempts to functionalize the methyl group in **25** (NBS, dibromantin; CrO_3. 3, 5-dimethylpyrozole; $KMnO_4$; Na_2CrO_7 either resulted in aromatic substitution, or removal of the N-4-methoxyphenylsulfonyl group.



18 **19**



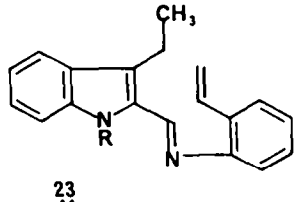
20 (R^1 = 4-$MeOC_6H_4SO_2$-; R^2 = CO_2Me)



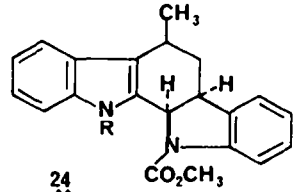
21 (R^3 = CHO)

22 (R^3 = Me)

From the above results it seems that a suitably substituted and protected tryptamine derivative, such as **26**, will provide the solution to introducing the correct functionality for constructing the lactam ring to complete the synthesis of the fused dimeric indole alkaloid staurosporinone **2**. We are currently investigating this problem.



23



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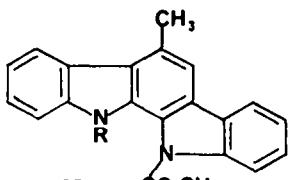
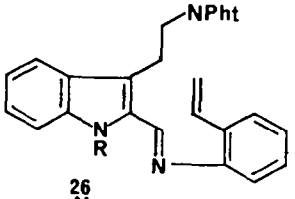
EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer grating spectrometer. UV spectra were recorded on a Perkin-Elmer 554 spectrometer, for solns in abs EtOH. ^{1}H NMR spectra were recorded on either a Varian EM-360 spectrometer, or Varian HR 220 MHz spectrometer. Elemental analyses



25



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were carried out by the Midwest Microlab, Indianapolis. Mp were taken on a Thomas–Hoover mp apparatus, and are uncorrected.

All solvents were dried and purified by standard techniques prior to use. All reactions were run under either N_2 or argon unless otherwise stated. TLC, for monitoring the progress of reactions was conducted with Merck GF_{254} silica gel, aluminum backed plates. Routine chromatographic purification of compounds was conducted using Merck silica gel 60-H (Cat. No. 7736) with a small hand bellows to develop a pressure gradient. Preparative layer chromatography (PLC) was carried out using Merck precoated plates, silica gel 60-F-254 (0.5 mm thickness).

1 - [(p - *Methoxyphenyl*)*sulfonyl*] - 3 - *methylindole* 9 (R^1 = Me). To a suspension of NaH (2.02 g 59.3% dispersion in mineral oil, washed with dry benzene) in dry THF (30 ml) at 5°, was added 3-methylindole (6.56 g 50 mmol) in dry THF (30 ml). After stirring at 5° for 15 min then 20° for 15 min followed by heating at reflux for 1 hr to ensure complete salt formation, *p*-methoxybenzenesulfonyl chloride (10.84 g 52.5 mmol) in dry THF (40 ml) was added dropwise. After 1 hr at 20° the above mixture was poured into water (100 ml) and extracted with EtOAc (3 × 100 ml). The combined extracts were washed with water (100 ml), and sat NaCl aq (50 ml), dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization of the residue gave **9** (R^1 = Me) (12.03 g 80%), m.p. 135–137° (from EtOAc/petrol). NMR ($CDCl_3$) δ 2.21 (3H, d, J = 1.5 Hz), 3.75 (3 H, s), 6.84 (2 H, d, J = 9 Hz), 7.18–7.53 (4 H, m), 7.78 (2 H, d, J = 9 Hz), 8.32 (1 H, dd, J = 6 Hz and 2.5 Hz). Calc for $C_{16}H_{15}NO_3S$. C, 63.77; H, 5.02; N, 4.65. (Found, C, 63.63; H, 5.08; N, 4.70%).

1 - [(p - *Methoxyphenyl*)*sulfonyl*] - 3 - *methyl* - 2 - *formylindole* **11** (R^1 = Me). To a soln of **9** (R^1 = Me) (3.01 g 10 mmol) in CH_2Cl_2 (20 ml) and α, α-dichloromethylmethyl ether (5.75 g 50 mmol) at −25° was added $SnCl_4$ (6 ml 50 mmole) in CH_2Cl_2 (10 ml), in one portion. After 2 hr at −25° a yellow ppt was formed. To the above mixture was added 1 N HCl (100 ml), and the mixture extracted with CH_2Cl_2 (2 × 50 ml). The extracts were washed with water (2 × 50 ml), and sat NaCl aq (50 ml), dried ($MgSO_4$) and evaporated *in vacuo*. Flash chromatography of the residue on silica gel 60, eluting with $CHCl_3$/petrol, gave the crude product which was recrystallized from $CHCl_3$/petrol to give **11** (R^1 = Me) (2.16 g 66%), m.p. 130–132° (from EtOAc/petrol). IR ($CHCl_3$ 1675 and 1600 cm^{-1}. NMR ($CDCl_3$) δ 2.50 (3 H, s), 3.75 (3 H, s), 6.78 (2 H, d, J = 9 Hz), 7.20–7.80 (5 H, m), 8.25 (1 H, d, J = 8 Hz), 10.67 (1 H, s). (Found, C, 61.91; H, 4.62; N, 4.29%. Calc for $C_{17}H_{15}NO_4S$. C, 61.99; H, 4.59; N, 4.25%).

1-[(p-*Methoxyphenyl*)*sulfonyl*]-3-*ethylindole* **10** (R^1 = Et). Using the same procedure as for **9** (R^1 = Me), except that 3-ethylindole (580 mg 4 mmol)[13] was used, gave **10** (R^1 = Et) (580 mg 70%), m.p. 121–122° (from EtOAc/hexane). IR ($CHCl_3$) 1601, 1576 and 1174 cm^{-1}. NMR ($CDCl_3$) δ 1.28 (3 H, t, J = 7 Hz), 2.66 (2 H, q, J = 7 Hz), 3.75 (3 H, s), 6.85 (2 H, d, J = 9 Hz), 7.36–7.18 (4 H, m), 7.47 (1 H, d, J = 9 Hz), 7.82 (2 H, d, J = 8 Hz), 7.98 (1 H, d, J = 8 Hz). (Found; C, 65.12; H, 5.47; N, 4.21%. Calc for $C_{17}H_{17}NO_3S$. C, 65.36; H, 5.48; N, 4.48%).

1-[(p-*Methoxyphenyl*)*sulfonyl*]-3-*ethyl*-2-*formylindole* **12** (R^1 = Et). To a soln of **10** (R^1 = Et) (624 mg 2 mmol) in CH_2Cl_2 (40 ml) and α, α-dichloromethylmethyl ether (1.15 g 10 mmol) at −35°, was added $TiCl_4$ (1.90 g 10 mmol) in CH_2Cl_2 (5 ml) in one portion. After 20 min the above mixture was poured into ice-water (50 ml) and stirred vigorously for 20 min. The mixture was extracted with CH_2Cl_2 (50 ml), and the extract washed with water (50 ml) and sat NaCl aq (50 ml), dried (Na_2SO_4) and evaporated *in vacuo*. The residue was crystallized from EtOAc–hexane to give **12** (R^1 = Et) (436 mg 64%). An addition quantity of **12** (R^1 = Et) (117 mg) was obtained by chromatography of the mother liquors to give a total yield of 81%, m.p. 152–153° (from EtOAc/hexane). IR ($CHCl_3$), 1675 and 1600 cm^{-1}. NMR ($CDCl_3$) δ 1.11 (3 H, t, J = 8 Hz), 3.00 (2 H, q, J = 8 Hz), 3.77 (3 H, s), 6.82 (2 H, d, J = 10 Hz), 7.68–7.50 (5 H, m), 8.16 (1 H, d, J = 8 Hz), 10.56 (1 H, s). (Found; C, 63.35; H, 5.21; N, 3.99%. Calc for $C_{18}H_{17}NO_4S$. C, 63.51; H, 5.03; N, 4.11%).

Methyl cis- 2, 3, 4, 4a, 5, 10b-*hexahydro*-10-[(p-*methoxyphenyl*)*sulfonyl*]-1 H-*pyrrolo* [2, 3-a]*carbazole*-1-*carboxylate* **14**. To a soln of **10** (R^1 = Me) (660 mg) in CH_2Cl_2 (25 ml) was added 3-butenylamine (480 mg) and the mixture stirred at 20° for 6 hr, 4 Å molecular sieves were added, and after 12 hr the suspension filtered through a celite pad. Evaporation of the filtrate *in vacuo* gave **13**, which was used directly.

A soln of the above imine (2 mmol) in dry chlorobenzene (20 ml) at 0° was treated with NPr^i_2Et (1.06 ml 6 mmol), followed by a soln of freshly distilled methyl chloroformate (568 mg 6 mmol) in chlorobenzene (2 ml). The mixture was stirred at 20° for 15 min then heated to reflux. After 1 hr the mixture was cooled to 20°, and evaporated *in vacuo*. Flash chromatography of the residue on silica gel 60 H gave **14** (633 mg) on elution with EtOAc/petrol. Recycling recovered imine **13** (295 mg) gave a further quantity of **14** (112 mg). Total yield of **14** (765 mg 84%), m.p. 150.5–152.5° (from EtOAc/petrol). IR ($CHCl_3$) 1670 and 1600 cm^{-1}. NMR ($CDCl_3$) δ 1.67–2.19 (4 H, m), 2.40–2.91 (4 H, m), 3.23–3.40 (1 H, m), 3.64 (3 H, s), 3.73 (3 H, s), 5.41 (1 H, d, J = 4 Hz), 6.82 (2 H, d, J = 9 Hz), 7.16–7.48 (3 H, m), 7.70 (2 H, d, J = 9 Hz), 8.07 (1 H, d, J = 8 Hz). (Found; C, 62.72; H, 5.60; N, 6.37%. Calc for $C_{23}H_{24}N_2O_5S$. C, 62.71; H, 5.49; N, 6.36%).

Methyl cis-2, 3, 4, 4a, 5, 10c-*hexahydro*-6-[(p-*methoxyphenyl*)*sulfonyl*]-1H-*pyrrolo*[3, 2-c]*carbazole*-1-*carboxylate* **16**. To a soln of **3** (990 mg 3 mmol) in dry benzene (20 ml) was added butenylamine (426 mg 6 mmol). After 6 hr at 20°, 4 Å molecular sieves were added and the mixture stirred for a further 12 hr. The suspension was filtered through a celite pad, and the filtrate evaporated *in vacuo* to give the crude imine **15**.

A soln of **15** (3.0 mmol) in dry chlorobenzene (15 ml) at 0° was treated with NPr^i_2Et (1.75 ml 10 mmol), followed by a soln of freshly distilled methyl chloroformate (950 mg 10 mmol) in chlorobenzene (5 ml). The mixture was heated to reflux for 5 hr cooled to 20° and evaporated *in vacuo*. Flash chromatography of the residue on silica gel 60 H, eluting with EtOAc/petrol (1:3) gave **16** (535 mg 40%), m.p. 158.5–159.5° (from MeOH). IR ($CHCl_3$) 1680 and 1595 cm^{-1}. NMR ($CDCl_3$) δ 1.70–2.14 (4 H, m), 2.48–2.66 (1 H, m), 2.82–3.25 (3 H, m), 3.45–3.68 (1 H, m), 3.77 (6 H, s), 5.25 (1 H, bd, J = 6 Hz), 6.86 (2 H, d, J = 9 Hz), 7.18–7.35 (3 H, m), 7.70 (2 H, d, J = 9 Hz), 8.18 (1 H, d, J = 7 Hz). (Found C, 62.40; H, 5.65; N, 5.99%. Calc for $C_{23}H_{24}N_2O_5S$. C, 62.71; H, 5.49; N, 6.36%).

Condensation between the aldehyde **11** (R^1 = Me) *and*

(E)-*methyl 2-aminocinnamate*. A soln of **11** (R^1 = Me) (343 mg 1 mmol) and methyl 2-aminocinnamate (195 mg 1.1 mmol) in benzene (50 ml) containing a catalytic amount of *p*-toluenesulfonic acid monohydrate, was heated at reflux for 8 hr with provision for the removal of water (Dean–Stark). The solvent was evaporated *in vacuo* and the residue crystallized from EtOAc–hexane to give **17** (490 mg 95%), m.p. 160–162°. IR ($CHCl_3$) 1700, 1690, 1621, 1605 cm^{-1}. NMR ($CDCl_3$) δ 2.60 (3 H, s), 3.72 (3 H, s), 3.77 (3 H, s), 6.51 (1 H, d, J = 17 Hz), 6.80 (2 H, d, J = 10 Hz), 7.54–7.16 (6 H, m), 7.60 (2 H, d, J = 10 Hz), 7.70 (1 H, d, J = 8 Hz), 8.23 (2 H, d, J = 8 Hz), 8.43 (2 H, d, J = 17 Hz), 9.23 (1 H, s).

Methyl cis- 5, 6, 6a, 11a-*tetrahydro*-12[(p-*methoxyphenyl*) *sulfonyl*]-11 H-*indolo*[2, 3-a]*carbazole*-11-*carboxylate* **19**. To a soln of **11** (R^1 = Me)(329 mg 1 mmol) in CH_2Cl_2 (15 ml) was added 2-aminostyrene (125 mg 1.05 mmol). Freshly activated 4 Å molecular sieves (*ca* 3 g) were added, and the mixture stirred at 20° for 48 hr. The mixture was filtered, and the solvent evaporated *in vacuo* to give a yellow solid. Crystallization from $CHCl_3$–hexane gave **18** (430 mg 97%), m.p. 162–163°. IR $CHCl_3$), 1612, 1595, 1166 cm^{-1}. NMR ($CDCl_3$) δ 2.55 (3 H, s), 3.64 (3 H, s), 5.32 (1 H, d, J = 12 Hz), 5.78 (1 H, d, J = 18 Hz), 6.72 (2 H, d, J = 9 Hz), 7.66–7.17 (11 H, br, m), 8.23 (1 H, d, J = 8 Hz), 9.09 (1 H, s).

To a soln of **18** (474 mg 1.1 mmol) in chlorobenzene (2 ml) was added methyl chloroformate (520 mg 5.5 mmol), and the mixture heated at 110° for 2 hr. The above soln was evaporated *in vacuo*, and the residue crystallized from EtOAc–hexane to give **19** (242 mg. 45%). Chromatography of the mother liquors gave an additional quantity of **19** (240 mg) making the total yield 89%, m.p. 177–179°. IR ($CHCl_3$) 1701, 1600 cm^{-1}. NMR ($CDCl_3$) δ 1.85 (2 H, m), 2.20 (1 H, m), 2.61 (2 H, t, J = 7 Hz), 3.72 (3 H, s), 3.75 (3 H, s), 6.15 (1 H, d, J = 7 Hz), 6.82 (2 H, d, J = 8 Hz), 7.10 (3 H, t, J = 9 Hz), 7.39–7.18 (4 H, m), 7.75–7.57 (4 H, m), 8.32 (1 H, d, J = 7 Hz). (Found; C, 66.49; H, 5.06; N, 5.79%. Calc for $C_{27}H_{24}N_2O_5S$. C, 66.38; H, 4.95; N, 5.73%).

Methyl 12[(p-*methoxyphenyl*)*sulfonyl*]-11 H-*indolo*[2, 3-a] *carbazole*-11-*carboxylate* **20**. To a soln of **19** (488 mg 1 mmol) in toluene (10 ml) was added DDQ (1.13 g 5 mmol) and the mixture heated at reflux for 8 hr. The mixture was evaporated *in vacuo*, and the residue flash chromatographed to give **20** (310 mg 64%), m.p. 217–218° (from EtOAc–hexane). IR ($CHCl_3$) 1730, and 1590 cm^{-1}. NMR ($CDCl_3$) δ 3.59 (3 H, s), 4.26 (3 H, s), 6.40 (2 H, d, J = 9 Hz), 6.94 (2 H, d, J = 9 Hz), 7.34 (1 H, t, J = 7 Hz), 7.45 (2 H, t, J = 7 Hz), 7.59 (1 H, t, J = 7 Hz), 7.77 (2 H, t, J = 7 Hz), 8.07 (2 H, d, J = 8 Hz), 8.26 (1 H, d, J = 8 Hz), 8.48 (1 H, m). λ_{max}^{EtOH} 206, 232, 288, 307 and 340 nm (ϵ = 21,000, 28,990, 13,670, 13,610 and 15,980 respectively). (Found; C, 66.67; H, 4.19; N, 5.68%. Calc for $C_{27}H_{20}N_2O_5S$. C, 66.93; H, 4.16; N, 5.78%).

Methyl cis-5, 6, 6a, 11a-*tetrahydro*-6-*methyl*-12 [(p-*methoxyphenyl*)*sulfonyl*]-11 H-*indolo*[2, 3-a]*carbazole*-11-*carboxylate* **24**. A soln of **12** (R^1 = Et) (343 mg 1 mmol) in CH_2Cl_2 (15 ml) was treated with 2-aminostyrene (125 mg 1.05 mmol) in the usual way to give **23** (462 mg) as a yellow foam. IR ($CHCl_3$) 1613 and 1597 cm^{-1}. NMR ($CDCl_3$) δ 1.24 (3 H, t, J = 7 Hz), 3.09 (2 H, q, J = 7 Hz), 3.52 (3 H, s), 5.33 (1 H, d, J = 11 Hz), 5.80 (1 H, d, J = 17 Hz), 6.79 (2 H, d, J = 8 Hz), 7.70–7.16 (11 H, bm), 8.24 (1 H, d, J = 8 Hz), 8.99 (1 H, s).

To a soln of **23** (444 mg 1 mmol) in chlorobenzene (4 ml) was added methyl chloroformate (520 mg 5.5 mmol), and the mixture heated at reflux for 6 hr. Evaporation of the solvent *in vacuo*, followed by flash chromatography of the residue gave **24** (404 mg 81%) as a foam. IR ($CHCl_3$), 1700 and 1601 cm^{-1}. This material was used directly in the dehydrogenation step.

Methyl 12[(p-*methoxyphenyl*)*sulfonyl*]-6-*methyl*-11 H-*indolo*[2, 3-a]*carbazole* - 11 - *carboxylate* **25**. To a soln of **24** (502 mg 1 mmol) in toluene (10 ml) was added DDQ (1.13 g 5 mmol) and the mixture heated at reflux for 10 hr. Evaporation *in vacuo* and flash chromatography of the residue gave **25** (320 mg 64%), m.p. 224–225° (from EtOAc–hexane). IR ($CHCl_3$) 1700, 1595, 1500 and 1205 cm^{-1}. NMR ($CDCl_3$) δ 2.76 (3 H, s), 3.55 (3 H, s), 4.12 (3 H, s), 6.39 (2 H, d, J = 9 Hz), 6.91 (2 H, d, J = 9 Hz), 7.51–7.24 (3 H, m), 7.56 (1 H, t, J = 8 Hz), 7.82 (1 H, s), 7.9 (1 H, d, J = 8 Hz), 8.04 (1 H, d, J = 8 Hz), 8.31 (1 H, d, J = 8 Hz), 8.49 (1 H, d, J = 9 Hz). (Found; C, 67.38; H, 4.49; N, 5.52%. Calc for $C_{28}H_{22}N_2O_5S$. C, 67.46; H, 4.51; N, 5.57%). λ_{max}^{EtOH} 214, 246, 274, 284, 306, 318, 340 nm (ϵ = 27500, 26450, 13670, 12840, 14390, 13460 and 3400 respectively.)

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