PREPARATION OF ALKYL-SUBSTITUTED INDOLES IN THE BENZENE PORTION. Part 4[1]

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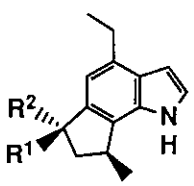
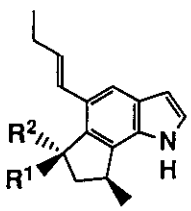
Abstract — A useful method for the preparation of variously substituted polyalkylindoles (**3b**) was established by H_2SO_4-catalyzed cyclization reaction of **1b**, where the substituent Y was designated as either the hydroxy or alkoxy group, to yield **3a** in good yields. The substrate (**1b**) was prepared from 1-phenylsulfonylpyrrole (**5**) by way of 1-phenylsulfonyl-2-pyrrolyl derivatives (**4**), *e. g.*, **6** and**13**, followed by the aldol reaction for the elongation of their carbonyl functions.

Biologically active natural products, trikentrins (*i. e.*, cis- and trans-trikentrins A, cis- and trans-trikentrins B, and iso-trans-trikentrin B) are constituents of an extract of the marine sponge *Trikentrion flabelliforme*, and have unique structural features of polyalkylindoles, whose substituents are only situated at the benzene portion of the indole nucleus (Scheme 1).[2,3] Aiming at the total synthesis of all of these trikentrins, we started preliminary experiments how to apply our indole formation reaction[1,4] to this problem and to establish at the same time a general synthetic methodology for complex substituted alkylindoles.

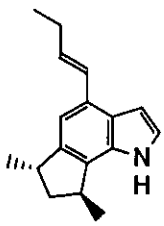


cis-trikentrin A
R^1= Me R^2= H



trans-trikentrin A
R^1= H R^2= Me

cis-trikentrin B
R^1= Me R^2= H

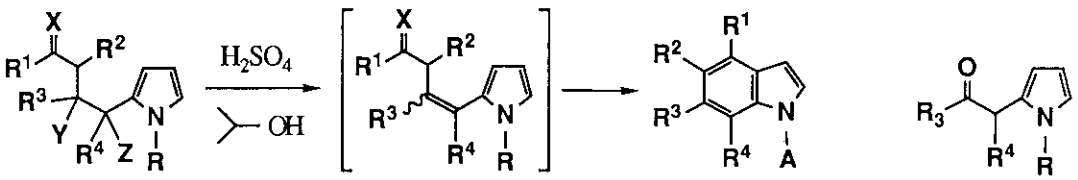


trans-trikentrin B
R^1= H R^2= Me

iso-trans-trikentrin B

Scheme 1

We have already noted that a compound having the structure (**1a**) afforded readily an indole derivative (**3a**) in good yield by treatment with H_2SO_4 in refluxing 2-propanol.[1,4b] Our plan in this report is to employ a structural variant (**1b**) of **1a** for the above cyclization reaction, since both **1a** and **1b** would produce the same intermediate (**2**) during the course of the indole formation (Scheme 2). Advantage to select the compound (**1b**) for a precursor to **3a** stems from the fact that we have our own preparative method[4a,5] to obtain the pyrrole derivative (**4**) from 1-phenylsulfonylpyrrole (**5**) and subsequent aldol reaction on **4** should produce **1b** easily. The aldol reaction could be attainable either by the Mukaiyama procedure[6] or by the Corey and Enders method.[7]



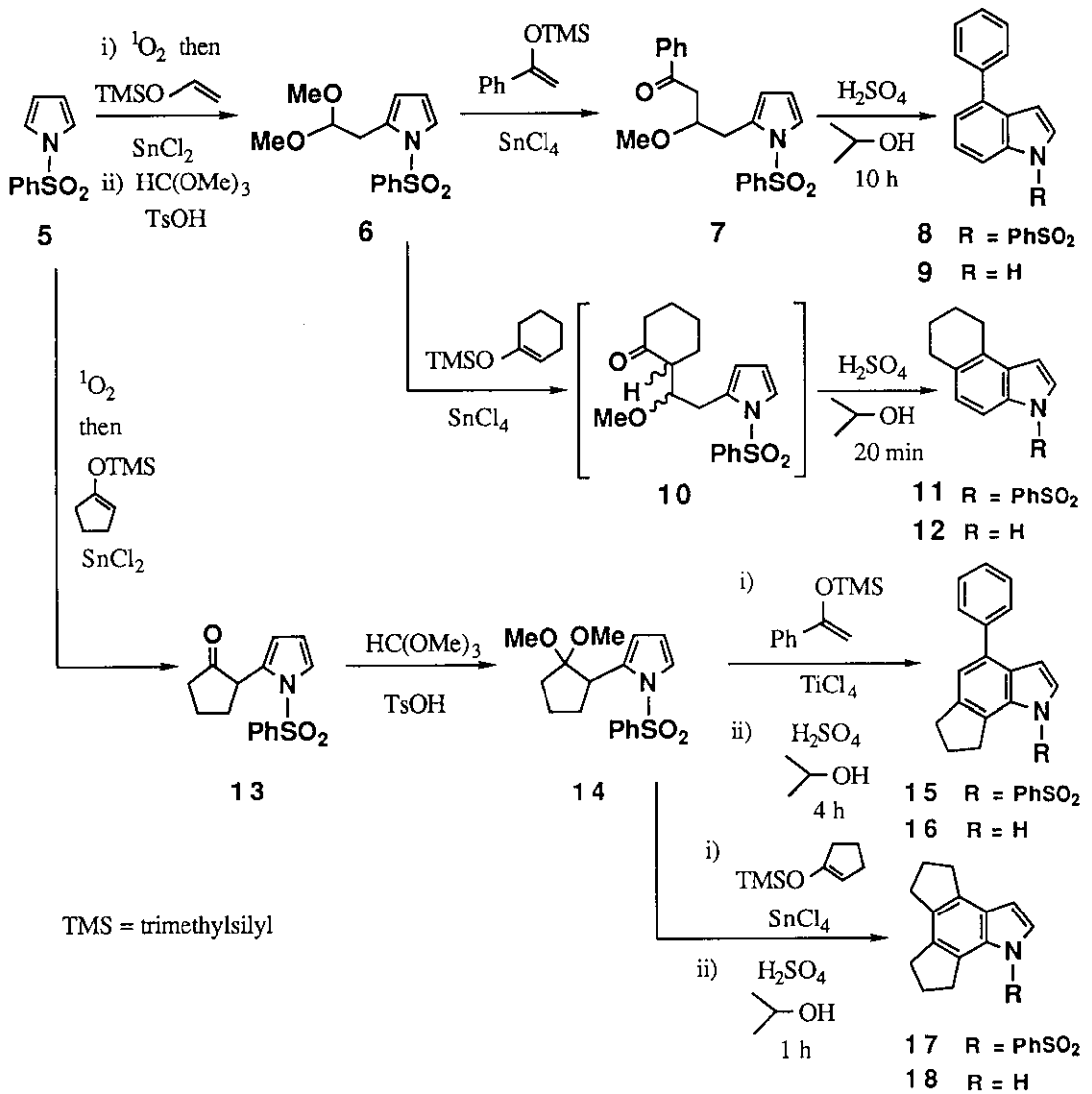
R= PhSO2 **X**= Ketone equivalent $\mathbf{R^5}$= H, alkyl group

Scheme 2

1-Phenylsulfonylpyrrole (**5**) was submitted to the photooxygenation reaction and the resulting mixture was treated with trimethylsilyl vinyl ether[8] or 1-trimethylsilyloxycyclopentene in the presence of $SnCl_2$ to afford (1-phenylsulfonyl-2-pyrrolyl)acetaldehyde or 2-(1-phenylsulfonyl-2-pyrrolyl)cyclopentanone (**13**) (71% yield) (Scheme 3). Both were then converted to their dimethyl acetals (**6** and **14**) in 46% (from **5**) and 86% yields, respectively. As the simplest example of **1b**, the compound (**7**) was prepared by treatment of **6** with α-trimethylsilyloxystyrene in the presence of $SnCl_4$[6] in 93% yield. Indole formation was carried out as reported before by refluxing **7** in 6% H_2SO_4-containing 2-propanol for 10 h and 4-phenyl-1-phenylsulfonylindole (**8**) was obtained in 82% yield.

In other cases where **1b** has various alkyl substituents more than two at R^1, R^2, R^3, and R^4, the molecule (**1b**) exists as a mixture of diastereomers. These are however changed to a single product during the next transformation affording an indole derivative (**3a**). Therefore the mixture (**10**) obtained from **6** was not separated to each diastereomer, and instead subjected directly to the indole-forming operation to give **11** in 74% yield from **6**. Similar sequence of reactions was applied to **14**, and phenylsulfonylindole derivatives

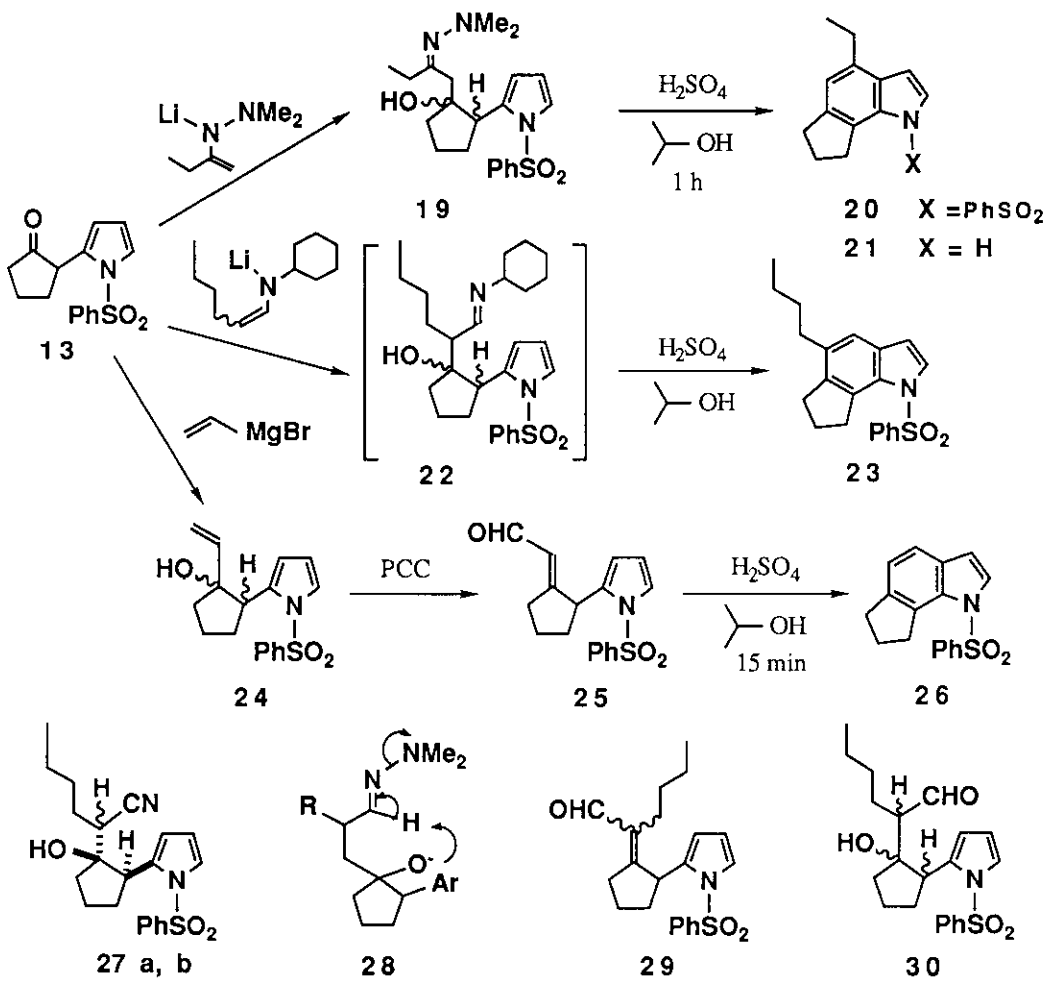
(**15** and **17**) were synthesized in 77% and 51% overall yields. The protecting group was removed either by Mg in MeOH[4b] (for **15**) or by alkaline hydrolysis (for **8**, **11**, and **17**), and indole derivatives (**9**, 12[9], **16**, and **18**) were obtained as rather unstable compounds in 97%, 99%, 80%, and 91% yields, respectively.



Scheme 3

Formation of **1b** from **13** was next examined by the aldol reaction using carbanion reagents (Scheme 4). Special care must be necessary here, since the carbonyl group of **13** is partially enolizable by the action of the reagents, so that the reaction should be carried out in a low polarity solvent. In the case of the Corey and

Enders reaction[7] utilizing the lithium salt of 2-butanone *N*, *N*-dimethylhydrazone,[10] a mixture of toluene and diethyl ether (1:1) was the solvent of choice and **19** was obtained in 61% yield, still accompanied by the recovery of **13** in 14% yield. Direct indole cyclization from the hydrazone (**19**) was successful, and the H_2SO_4 treatment as above afforded **20** in 84% yield. A model compound (**21**) for cis- and trans-trikentrins A as well as iso-trans-trikentrin B was thus synthesized by reductive cleavage (Mg in MeOH) of phenylsulfonyl group from **20** in 92% yield.



Scheme 4

On the other hand, application of the lithium salt of hexanal *N*, *N*-dimethylhydrazone to **13**, followed by the H_2SO_4 treatment of the resulting mixture afforded two epimers of the cyano compounds (**27a** and **27b**,

whose stereochemistry was undetermined) as major products in 28% and 17% yields. The expected compound (**23**) was isolated in 30% yield, accompanied by the 8% recovery of **13**. Presumably abstraction of the hydrogen at the aldehyde hydrazone took place intramolecularly as shown in the structure (**28**) and concomitant elimination of the dimethylamino group ended with the formation of the cyano function to give **27**.

The Wittig's directed aldol condensation[11] is the alternative method to elongate the carbonyl group of **13**. The lithium salt of hexanal *N*-cyclohexylimine[12] was reacted on **13**, and without separation of **22** the resulting mixture was submitted to the H_2SO_4 cyclization reaction. Separation of the products over silica gel revealed that the desired **23** was obtained only in a small amount, and majority was the aldehyde derivatives (**29** and **30**) and the recovery of **13** (37% yield). Therefore the combined aldehydes were treated again with H_2SO_4 and finally **23** was collected in 35% yield. These phenomena suggested that some unidentified materials having structures relating to **22** remained intact in the H_2SO_4 – 2-propanol conditions but they were hydrolyzed readily by the moisture of silica gel to afford **29** and **30**. Once these aldehydes were formed, the indole cyclization was effected quite easily. The compound (**23**) served as a model for cis- and trans-trikentrins B, and actual synthesis of the natural products was achieved by taking account of this fact.[13]

The Grignard reaction on **13** proceeded sluggishly. A simple reagent such as vinylmagnesium bromide could add to the carbonyl group only in a solvent of toluene – THF (*ca.* 3 : 1) to give **24** in 55% yield, accompanied by the inevitable recovery of **13** in 24% yield. The tertiary alcohol (**24**) was oxidized to **25** with pyridinium chlorochromate,[14] and the indole cyclization reaction afforded readily **26** in 77% yield.

EXPERIMENTAL

For the general description and others, refer to that in the preceding paper.

1-Phenylsulfonyl-2-pyrrolylacetaldehyde Dimethyl Acetal (6)— According to the reported procedure,[4a,5] a solution of 1-phenylsulfonylpyrrole (**5**) (840 mg) and methylene blue (42 mg) in CH_2Cl_2 (100 ml) was photooxygenated at -55 – -60°C for 2 h. To this was added successively a CH_2Cl_2 (5 ml) solution of crude trimethylsilyl vinyl ether[8] (943 mg, containing about 350 mg of chlorltrimethylsilane), and an EtOAc (40 ml) solution of $SnCl_2$ (925 mg), and the mixture was stirred at -78°C for 1 h and at 0°C for 1.5 h to give the residue (1.2 g) after the reported work-up. A MeOH (3 ml) solution of the residue, trimethyl orthoformate (3 ml), and *p*-TsOH·H_2O (42 mg) was stirred at room temperature for 4 h, and the mixture was quenched with sat. $NaHCO_3$-H_2O, and extracted with CH_2Cl_2. Usual work-up followed by chromatography [hexane-EtOAc (9:1)] afforded the recovery of **5** (95 mg, 11%) and the product (**6**) (552 mg, 46%), colorless oil. Ms *m/z*: 295 (M^+). Nmr ($CDCl_3$) δ: 2.99 (2H, d, J=5.5 Hz), 3.23 (6H, s), 4.51 (1H, t,

J=5.5 Hz), *ca.* 6.06-6.19 (1H, m), 6.19 (1H, dd, J=3.5, 3.5 Hz), 7.28 (1H, dd, J=3.5, 2 Hz), 7.33-7.60 (3H, m), 7.60-7.85 (2H, m).

2-(1-Phenylsulfonyl-2-pyrrolyl)cyclopentanone (13) — Applying the reported procedure,[4a,5] **5** (1.800 g), 1-trimethylsilyloxycyclopentenone (1.630 g), and $SnCl_2$ (1.980 g) afforded **13** (1.779 g, 71%) as colorless prisms, mp 73.5-74.5°C (MeOH-H_2O). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.29; H, 5.16, N, 4.78. Ms *m/z*: 289 (M^+). Ir (KBr) cm^{-1}: 1740. Nmr ($CDCl_3$) δ: 1.40-2.60 (6H, m), 3.90 (1H, br dd, J=9, 9 Hz), 5.96 (1H, dd, J=3.5, 1.5 Hz), 6.19 (1H, dd, J=3.5, 3.5 Hz), 7.19 (1H, dd, J=3.5, 1.5 Hz), 7.25-7.62 (3H, m), 7.62-7.87 (2H, m).

2-(1-Phenylsulfonyl-2-pyrrolyl)cyclopentanone Dimethyl Acetal (14) — A MeOH (3 ml) solution of **13** (100.5 mg), trimethyl orthoformate (0.5 ml), and *p*-TsOH·H_2O (8 mg) was stirred at room temperature for 45 min. Addition of sat. $NaHCO_3$-H_2O, extraction with CH_2Cl_2, usual work-up, and ptlc [hexane- EtOAc (6:1)] gave **14** (100 mg, 86%), colorless syrup. Ms *m/z*: 335 (M^+). Nmr ($CDCl_3$) δ: 1.21-2.09 (6H, m), 2.82 (3H, s), 3.33 (3H, s), 3.58-3.85 (1H, m), 6.21 (2H, d, J=3 Hz), 7.31 (1H, dd, J=3, 3 Hz), *ca.* 7.38-7.67 (3H, m), 7.67-7.93 (2H, m).

3-Methoxy-1-phenyl-4-(1-phenylsulfonyl-2-pyrrolyl)-1-butanone (7) — To a solution of **6** (93 mg) and α-trimethylsilyloxystyrene (187 mg, 97% purity) in CH_2Cl_2 (3.5 ml) was added $SnCl_4$ (75 μl) at -70°C under Ar atmosphere. After stirring at that temperature for 15 min, sat. $NaHCO_3$-H_2O was added, and the mixture was filtered through a celite bed and treated as usual. Purification by ptlc [hexane-EtOAc (4:1)] afforded **7** (112 mg, 93%), colorless syrup. Ms *m/z*: 383 (M^+). Ir ($CHCl_3$) cm^{-1}: 1680. Nmr ($CDCl_3$) δ: 2.74-3.41 (4H, m), 2.92 (3H, s), 3.99-4.32 (1H, m), 6.06-6.18 (1H, m), 6.18 (1H, dd, J=3.5, 3.5 Hz), 7.27 (1H, dd, J=3.5, 2 Hz).

4-Phenyl-1-phenylsulfonylindole (8) — Reflux of **7** (60 mg) in 6% H_2SO_4 – 2-propanol (4.5 ml) for 10 h, work-up as reported previously,[1,4b] and purification by ptlc [hexane-EtOAc (14:1)] gave **8** (43 mg, 82%) as colorless syrup. Hrms Calcd for $C_{20}H_{15}NO_2S$: 333.082. Found: 333.081. Nmr ($CDCl_3$) δ: 6.72 (1H, d, J=4 Hz), 7.61 (1H, d, J=4 Hz), 7.68-8.05 (3H, m). Preparation of **11**, **15**, and **17** was carried out analogously from **6** and **14** without identification of the intermediary ketone derivatives such as **10** in the yields of 74%, 77%, and 51%.

1-Phenylsulfonyl-4,5,6,7-tetrahydrobenz[*e*]indole (11) — Colorless prisms, mp 183.5-184.5°C (CH_2Cl_2-MeOH). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.50. Found: C, 69.37; H, 5.51; N, 4.67. Ms *m/z*: 311 (M^+). Nmr ($CDCl_3$) δ: 1.60-2.00 (4H, m), 2.58-2.98 (4H, m), 6.56 (1H, d, J=4 Hz), 6.96 (1H, d, J=8.5 Hz), 7.18-7.57 (3H, m), 7.45 (1H, d, J=4 Hz), 7.68 (1H, d, J=8.5 Hz), 7.68-7.94 (2H, m).

4-Phenyl-1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (15) — Colorless syrup. Hrms Calcd for $C_{23}H_{19}NO_2S$: 373.114. Found: 373.113. Nmr ($CDCl_3$) δ: 2.03 (2H, tt, J=7, 7 Hz), 2.97 (2H, t, J=7 Hz), 3.22 (2H, t, J=7 Hz), 6.79 (1H, d, J=4 Hz), 7.17 (1H, s), 7.61-7.85 (2H, m), 7.69 (1H, d, J=4 Hz).

1-Phenylsulfonyl-4*H*-1,5,6,7,8,9-hexahydrobiscyclopent[*e*,*g*]indole (17) — Colorless needles, mp 109-111°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68; N, 4.15. Found: C, 71.36; H, 5.64; N, 4.21. Ms *m/z*: 337 (M^+). Nmr ($CDCl_3$) δ: 1.98 (2H, tt, J=7, 7 Hz), 2.11

(2H, tt, J=7, 7 Hz), 2.78 (2H, t, J=7 Hz), 2.82 (2H, t, J=7 Hz), 2.99 (2H, t, J=7 Hz), 3.15 (2H, t, J=7 Hz), 6.56 (1H, d, J=4 Hz), 7.18-7.51 (3H, m), 7.61 (1H, d, J=4 Hz), 7.61-7.76 (2H, m).

4-Phenyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (16) — By the usual treatment[4b] of **15** (29 mg) with Mg (37 mg) in MeOH (3 ml) at room temperature for 4 h, **16** (14.5 mg, 80%) was obtained as unstable colorless oil after purification by ptlc [hexane-EtOAc (9:1)]. Ms *m/z*: 233 (M^+). Nmr ($CDCl_3$) δ: 2.02 (2H, tt, J=7, 7 Hz), 3.02 (2H, t, J=7 Hz), 3.07 (2H, t, J=7 Hz), 6.65 (1H, dd, J=3.5, 2 Hz), 7.00-7.20 (2H, m), 7.20-7.55 (3H, m), 7.55-7.76 (2H, m), 7.91 (1H, br s).

Alkaline Hydrolysis of 8, 11, and 17 — Usual treatment[1,4b] with 10% KOH in DME-MeOH-H_2O (2:1:1) at 50°C for 5 h for **8**, at 60°C for 5 h for **11**, and at 85-90°C for 6 h for **17** affoded **9**, **12**, and **18** in 97%, 99%, and 91% yields. **4-Phenylindole (9)**: Colorless crystals, mp 58-60°C. (Attempted recrystallization from various solvents proved unsuccessful). Hrms Calcd for $C_{14}H_{11}N$: 193.089. Found: 193.092. Nmr ($CDCl_3$) δ: 6.64 (1H, dd, J=3, 2.5 Hz), 7.04 (1H, dd, J=3, 3 Hz), *ca.* 7.08-7.54 (6H, m), 7.54-7.75 (2H, m), 7.96 (1H, br s). **4,5,6,7-Tetrahydrobenz[*e*]indole (12)**[9]: Colorless needles, mp 95-97°C, (MeOH-H_2O). Hrms Calcd for $C_{12}H_{13}N$: 171.105. Found: 171.106. Nmr ($CDCl_3$) δ: 1.60-2.06 (4H, m), 2.63-3.10 (4H, m), 6.38-6.51 (1H, m), 6.86 (1H, d, J=8.5 Hz), 7.06 (1H, dd, J=3, 3 Hz), 7.09 (1H, d, J=8.5 Hz), 7.94 (1H, br s). **4*H*-1,5,6,7,8,9-Hexahydrobiscyclopent[*e*,*g*]indole (18)**: Colorless needles, mp 166-167°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.67; N, 7.10. Found: C, 85.47; H, 7.68; N, 7.01. Ms *m/z*: 197 (M^+). Nmr ($CDCl_3$) δ: 1.97-2.04 (4H, m), 2.73-3.23 (8H, m), 6.42 (1H, dd, J=3.5, 2 Hz, changed to d, J=3.5 Hz with D_2O), 7.07 (1H, dd, J=3.5, 2.5 Hz, changed to d, J=3.5 Hz with D_2O), 7.86 (1H, br s).

Formation of 19 from 13 — An Et_2O solution (2 ml) of 2-butanone *N*, *N*-dimethylhydrazone[10] (159 mg) was treated with 15% BuLi in hexane (0.71 ml) at -73 – -60°C for 1 h under Ar atmosphere. To this was added dropwise a toluene solution (2 ml) of **13** (40 mg) and the resulting mixture was stirred at -60 – -40°C for 2.5 h. Quenching with sat. NH_4Cl-H_2O, extraction with Et_2O, usual work-up, and ptlc [hexane-EtOAc (3:1)] afforded the recovered **13** (5.5 mg, 14%) and **19** (34 mg, 61%), colorless syrup. Hrms Calcd for $C_{21}H_{29}N_3O_3S$: 403.193. Found: 403.194. Nmr of the major isomer ($CDCl_3$) δ: 1.01 (3H, t, J=7 Hz), 1.94 (1H, d, J=13.5 Hz), 2.29 (6H, s), 2.60 (1H, d, J=13.5 Hz), 3.11-3.45 (1H, m), 6.26 (1H, dd, J=3.5, 3.5 Hz), 6.49 (1H, dd, J=3.5, 2 Hz), 7.31 (1H, dd, J=3.5, 2 Hz).

4-Ethyl-1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (20) — Refluxing **19** (34 mg) in 6% H_2SO_4 – 2-propanol (6 ml) for 1 h as above, and purification by ptlc [hexane-EtOAc (12:1)] afforded **20** (23 mg, 84%), colorless syrup. Ms *m/z*: 325 (M^+). Nmr ($CDCl_3$) δ: 1.26 (3H, t, J=7.5 Hz), 2.80 (2H, q, J=7.5 Hz), 2.80 (2H, tt, J=7, 7 Hz), 2.89 (2H, t, J=7 Hz), 3.14 (2H, t, J=7 Hz), 6.69 (1H, d, J=4 Hz), 6.96 (1H, s), 7.21-7.58 (3H, m), 7.58-7.78 (2H, m), 7.63 (1H, d, J=4 Hz).

4-Ethyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (21) — A MeOH solution (3 ml) of **20** (23 mg) was treated as above with Mg (42.5 mg) for 20 h. Ptlc [hexane-EtOAc (19:1)] afforded unstable crystalline **21** (12 mg, 92%), which was recrystallized from hexane at 0°C to give slightly purple prisms, mp 51-52°C. Ms *m/z*: 185 (M^+). Nmr ($CDCl_3$) δ: 1.31 (3H, t, J=7.5 Hz), 2.15 (2H, tt, J=7, 7 Hz), 2.71-3.13 (6H, m), 6.53 (1H, dd, J=3.5, 2 Hz, changed to d, J=3.5 Hz with D_2O), 6.84 (1H, s), 7.03 (1H, dd, J=3.5, 3.5 Hz, changed to d, J=3.5 Hz with D_2O), 7.83 (1H, br s).

Hexanal *N*, *N*-Dimethylhydrazone — According to the literature,[7] this was prepared in 89% yield as colorless oil, bp 95-96°C/42 mmHg. Ir (neat) cm^{-1}: 1610. Nmr ($CDCl_3$) δ: 0.88 (3H, t, J=6 Hz), 1.11-1.67 (6H, m), 2.06-2.37 (1H, m), 2.70 (6H, s), 6.63 (1H, t, J=5.5 Hz).

5-(1-Butyl)-1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopent[*g*]indole (23) — (i) To a solution of LDA, prepared from diisopropylamine (0.39 ml) and 15% BuLi – hexane (1.42 ml) in THF (3 ml) under Ar atmosphere at -20°C for 10 min, a THF solution (1.5 ml) of hexanal *N*, *N*-dimethylhydrazone (354 mg) was added and the mixture was stirred at 0°C for 30 min. It was cooled to -77°C and a toluene solution (4.5 ml) of **13** (78 mg) was added. After being stirred at -77 – -59°C for 1.5 h, this was quenched with sat. NH_4Cl-H_2O, and extraction with CH_2Cl_2, usual work-up and ptlc [benzene-EtOAc (6:1)] afforded a mixture of products (133 mg), which was then exposed to reflux with 6% H_2SO_4 in 2-propanol (6 ml) as above for 1 h. Usual treatment and ptlc [benzene-EtOAc (14:1)] gave three products, **23** (29 mg, 30%), **27a** (29 mg, 28%, less polar isomer), and **27b** (18 mg, 17%, more polar isomer), along with the recovery of **13** (6 mg, 8%). The desired **23**: Colorless prisms, mp 85-86°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{21}H_{23}NO_2S$: C, 71.35; H, 6.56; N, 3.96. Found: C, 71.33; H, 6.59; N, 4.04. Ms *m/z*: 353 (M^+). Nmr ($CDCl_3$) δ: 0.90 (3H, dif t, J=6.5 Hz), 1.12-1.77 (4H, m), 2.00 (2H, tt, J=7.5, 7.5 Hz), 2.43-2.73 (2H, m), 2.86 (2H, t, J=7.5 Hz), 3.20 (2H, t, J=7.5 Hz), 6.59 (1H, d, J=4 Hz), 7.14 (1H, s), 7.19-7.80 (5H, m), 7.59 (1H, d, J=4 Hz). The cyano compound (**27a**): Colorless syrup. Ms *m/z*: 386 (M^+). Ir ($CHCl_3$) cm^{-1}: 2240. Nmr ($CDCl_3$) δ: 0.86 (3H, dif t, J=6 Hz), 1.80 (1H, s, OH), 2.58-2.91 (1H, m), 3.49-3.81 (1H, m), 6.21-6.45 (2H, m). The cyano compound (**27b**): Colorless syrup. Ms *m/z*: 386 (M^+). Ir ($CHCl_3$) cm^{-1}: 2245. Nmr ($CDCl_3$) δ: 2.07 (1H, s, OH), 2.53-2.82 (1H, m), 3.44-3.80 (1H, m), 6.31 (2H, d, J=2.5 Hz), 7.39 (1H, dd, J=3.5, 3.5 Hz), *ca.* 7.39-7.80 (5H, m).

(ii) To a stirred solution of LDA, prepared from diisopropylamine (0.20 ml) and 15% BuLi – hexane (0.80 ml) in THF (2 ml) under Ar atmosphere at -20°C for 10 min, a THF solution (1.5 ml) of hexanal cyclohexylimine[12] (226 mg) was added, and the mixture was stirred at -20°C for 45 min and at 0°C for 15 min. It was cooled to -73°C, a toluene solution (3.5 ml) of **13** (60 mg) was added dropwise, and stirring was continued at -73 – -63°C for 1 h. Addition of sat. NH_4Cl-H_2O and sat. $NaHCO_3$-H_2O, extraction with Et_2O, and usual work-up gave a residue (283 mg), which was treated with 6% H_2SO_4 – 2-propanol (9 ml) at reflux for 0.5 h. Usual treatment as above and purification by ptlc [hexane-EtOAc (9:1), and then hexane-CH_2Cl_2 (1:1)] afforded **23** (8 mg), **29** (8 mg), **30** (18 mg, a mixture of two diastereomers), and the recovered **13** (22 mg, 37%). The combined **29** and **30** was treated again with 6% H_2SO_4 – 2-propanol (3 ml) as above to afford an additional crop of **23** (19 mg). Recrystallization of the combined **23** (27 mg) from CH_2Cl_2-hexane gave colorless prisms (26 mg, 35%), mp 85-86°C, which was identified as the above sample by comparison of ir and nmr spectra. The enal compound (**29**): Colorless syrup. Nmr ($CDCl_3$) δ, 0.87 (3H, dif t, J=6 Hz), 4.50-4.68 (1H, m), 5.59-5.73 (1H, m) 6.12 (1H, dd, J=3.5, 3.5 Hz), 7.30 (1H, dd, J=3.5, 2 Hz), *ca.* 7.30-7.86 (5H, m), 8.61 (1H, s). The hydroxy aldehyde derivative (**30**): Colorless syrup. Nmr ($CDCl_3$) δ: 2.10 (minor) and 2.57 (major isomers) (s each, OH), 2.29-2.66 (1H, m), 3.37-3.67 (1H, m), 6.16-6.36 (2H, m), 9.59 (minor) and 9.66 (major isomers) (d each, J=3.5 Hz).

2-(1-Phenylsulfonyl-2-pyrrolyl)-1-vinylcyclopentanol (24) — A toluene solution (3 ml) of **13** (112 mg) was treated with a 0.75 *M* solution of vinylmagnesium bromide in THF (1.00 ml) at -20°C for 10 min. Sat. NH_4Cl-H_2O was added and the mixture was extracted with Et_2O. Usual work-up and ptlc

[hexane-EtOAc (4:1)] afforded **13** (27 mg, 24%) and **24** (67 mg, 55%), colorless prisms, mp 109-110°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.29; H, 6.03; N, 4.41. Ms *m/z*: 317 (M^+). Ir (KBr) cm^{-1}: 1636. Nmr ($CDCl_3$) δ: 3.46-3.76 (1H, m), 4.80 (1H, dd, J=10.5, 1 Hz), 4.99 (1H, d, J=17.5, 1 Hz), 5.85 (1H, dd, J=17.5, 10.5 Hz), 6.23 (1H, dd, J=3.5, 3.5 Hz), 6.29 (1H, dd, J=3.5, 2.5 Hz), 7.28 (1H, dd, J=3.5, 2.5 Hz).

2-(1-Phenylsulfonyl-2-pyrrolyl)cyclopentylideneacetaldehyde (25) — A solution of **24** (40 mg) in CH_2Cl_2 (3 ml) was oxidized with PCC (543 mg) at room temperature for 2 h. The work-up as described in the literature[14] and ptlc [hexane-EtOAc (3:1)] gave **24** (23 mg, 58%) and **25** (10 mg, 25%), colorless syrup. Ms *m/z*: 315 (M^+). Ir ($CHCl_3$) cm^{-1}: 1667. Nmr ($CDCl_3$) δ: 4.10-4.40 (1H, m), 5.38 (1H, dddd, J=7.5, 2.5, 2.5, 2.5 Hz), 5.39 (1H, dd, J=3.5, 2 Hz), 6.23 (1H, dd, J=3.5, 3.5 Hz), 7.31 (1H, dd, J=3.5, 2 Hz), 9.78 (1H, d, J=7.5 Hz).

1-Phenylsulfonyl-1,6,7,8-tetrahydrocyclopent[g]indole (26) — Treatment of **25** (33 mg) with 6% H_2SO_4 in 2-propanol (4.5 ml) was carried out as above for 15 min. Usual work-up and ptlc [hexane-EtOAc (19:1)] gave **26** (24 mg, 77%) as colorless prisms, mp 133-134°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.53; H, 5.16; N, 4.70. Ms *m/z*: 297 (M^+). Nmr ($CDCl_3$) δ: 1.99 (2H, tt, J=7.5, 7.5 Hz), 2.91 (2H, t, J=7.5 Hz), 3.18 (2H, t, J=7.5 Hz), 6.64 (1H, d, J=3.5 Hz), 7.10 (1H, d, J=7.5 Hz), 7.31 (1H, d, J=7.5 Hz), 7.31-7.55 (3H, m), 7.55-7.83 (2H, m), 7.63 (1H, d, J=3.5 Hz).

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