

PREPARATION OF ALKYL-SUBSTITUTED INDOLES IN THE BENZENE
PORTION. Part 4¹

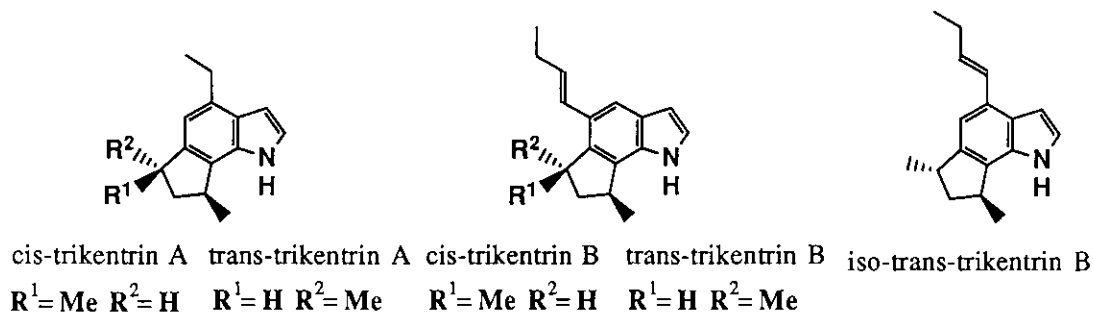
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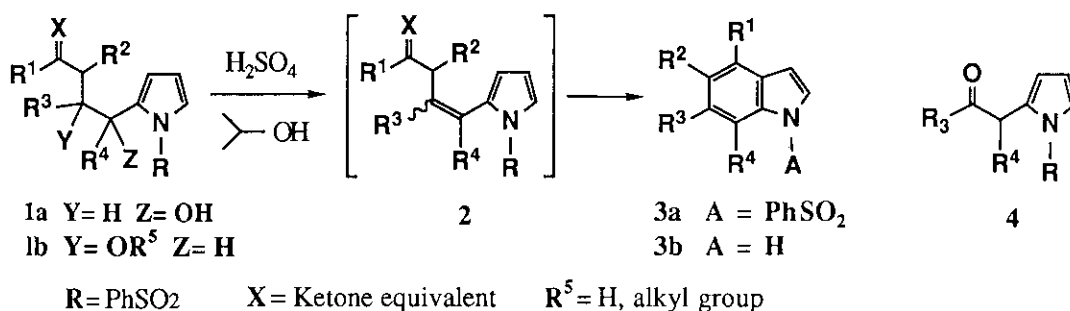
Abstract — A useful method for the preparation of variously substituted polyalkylindoles (**3b**) was established by H₂SO₄-catalyzed cyclization reaction of **1b**, where the substituent Y was designated as either the hydroxy or alkoxy group, to yield **3a** in good yields. The substrate (**1b**) was 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, trikentrin (*i. e.*, cis- and trans-trikentrin A, cis- and trans-trikentrin 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 trikentrin, 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.



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 procedure⁶ or by the Corey and Enders method.⁷

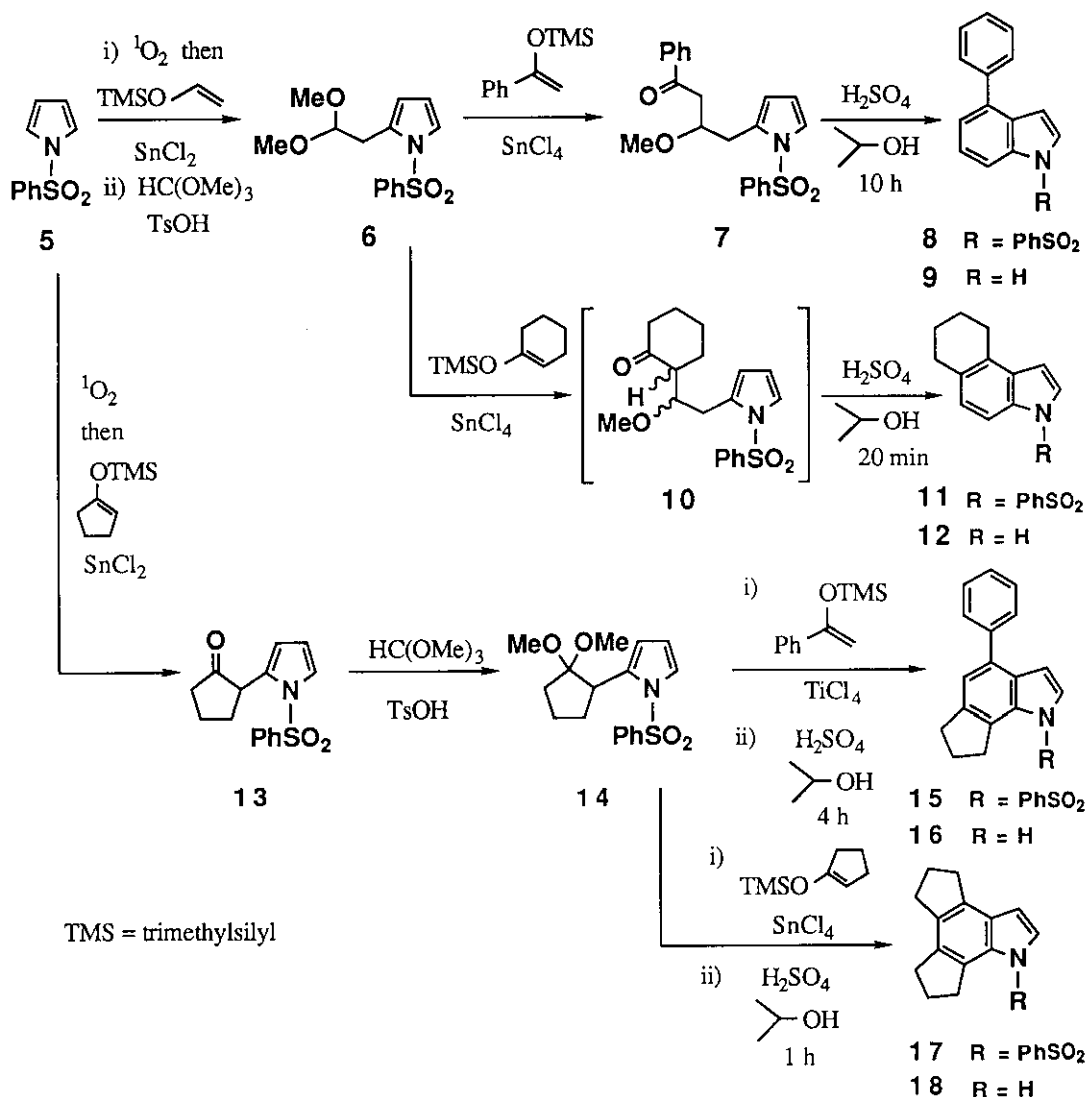


Scheme 2

1-Phenylsulfonylpyrrole (**5**) was submitted to the photooxygenation reaction and the resulting mixture was treated with trimethylsilyl vinyl ether⁸ 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 R¹, R², R³, and R⁴, 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

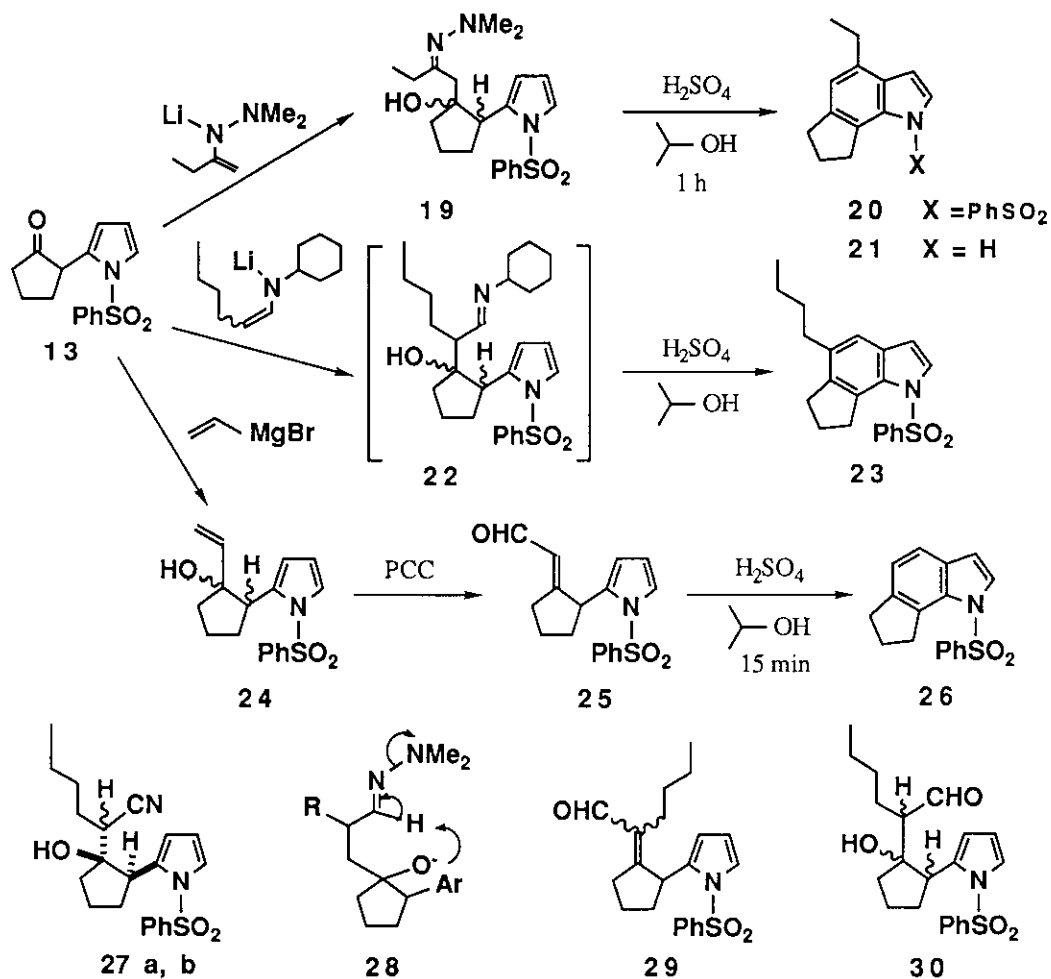
(15 and 17) were synthesized in 77% and 51% overall yields. The protecting group was removed either by Mg in MeOH^{4b} (for 15) or by alkaline hydrolysis (for 8, 11, and 17), and indole derivatives (9, 12⁹, 16, and 18) were obtained as rather unstable compounds in 97%, 99%, 80%, and 91% yields, respectively.



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 reaction⁷ 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 H₂SO₄ 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 H₂SO₄ 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 condensation¹¹ is the alternative method to elongate the carbonyl group of **13**. The lithium salt of hexanal *N*-cyclohexylimine¹² was reacted on **13**, and without separation of **22** the resulting mixture was submitted to the H₂SO₄ 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 H₂SO₄ and finally **23** was collected in 35% yield. These phenomena suggested that some unidentified materials having structures relating to **22** remained intact in the H₂SO₄ – 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 CH₂Cl₂ (100 ml) was photooxygenated at -55 – -60°C for 2 h. To this was added successively a CH₂Cl₂ (5 ml) solution of crude trimethylsilyl vinyl ether⁸ (943 mg, containing about 350 mg of chlorotrimethylsilane), and an EtOAc (40 ml) solution of SnCl₂ (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·H₂O (42 mg) was stirred at room temperature for 4 h, and the mixture was quenched with sat. NaHCO₃·H₂O, and extracted with CH₂Cl₂. 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 (CDCl₃) 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-H₂O). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$: 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-H₂O (8 mg) was stirred at room temperature for 45 min. Addition of sat. NaHCO_3 -H₂O, 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 -H₂O 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 $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}$: 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 $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{S}$: 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 $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{S}$: 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-4H-1,5,6,7,8,9-hexahydrobiscyclopent[e,g]indole (17) — Colorless needles, mp 109-111°C (CH_2Cl_2 -hexane). Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{S}$: 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-H₂O (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** afforded **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-H₂O). 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). **4H-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 Et₂O solution (2 ml) of 2-butanone *N,N*-dimethylhydrazone¹⁰ (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 -H₂O, extraction with Et₂O, 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. $\text{NH}_4\text{Cl-H}_2\text{O}$, 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 $\text{C}_{21}\text{H}_{23}\text{NO}_2\text{S}$: 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 cyclohexylimine¹² (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. $\text{NH}_4\text{Cl-H}_2\text{O}$ and sat. $\text{NaHCO}_3\text{-H}_2\text{O}$, 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. $\text{NH}_4\text{Cl-H}_2\text{O}$ 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 (CH₂Cl₂-hexane). Anal. Calcd for C₁₇H₁₉NO₃S: 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 (CDCl₃) 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 CH₂Cl₂ (3 ml) was oxidized with PCC (543 mg) at room temperature for 2 h. The work-up as described in the literature¹⁴ and ptlc [hexane-EtOAc (3:1)] gave **24** (23 mg, 58%) and **25** (10 mg, 25%), colorless syrup. Ms *m/z*: 315 (M⁺). Ir (CHCl₃) cm⁻¹: 1667. Nmr (CDCl₃) 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% H₂SO₄ 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 (CH₂Cl₂-hexane). Anal. Calcd for C₁₇H₁₅NO₂S: 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 (CDCl₃) 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).

ACKNOWLEDGMENT

Authors' thanks are due to Research Laboratories, Shionogi & Co. Ltd., for the measurement of elemental analysis. This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, which is gratefully acknowledged.

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Received, 6th February, 1990