PREPARATION OF ALKYL-SUBSTITUTED INDOLES IN THE BENZENE PORTION. Part 3[1]

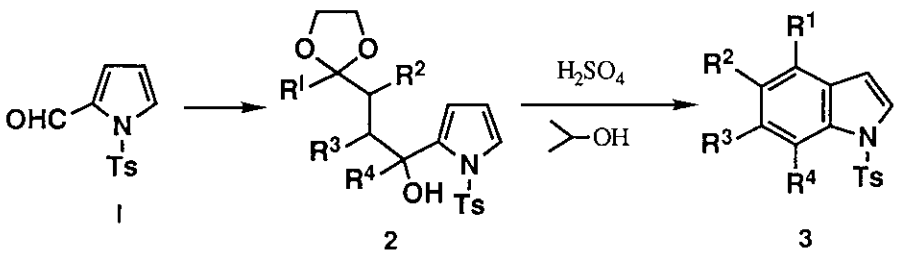
Hideaki Muratake and Mitsutaka Natsume*

Research Foundation Itsuu Laboratory

2-28-10 Tamagawa, Setagaya-ku, Tokyo 158, Japan

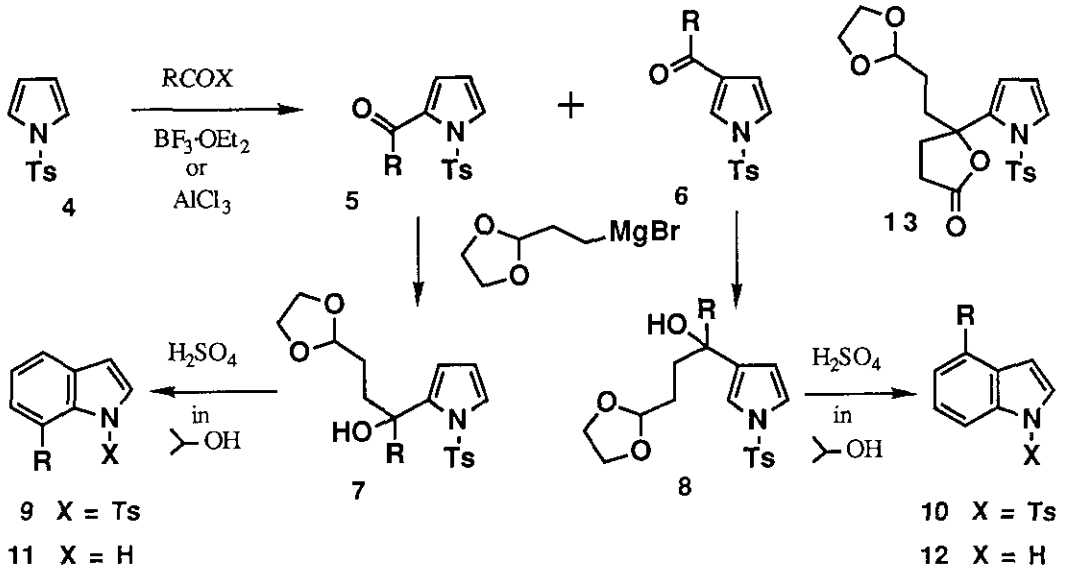
Abstract — Three-step synthesis of 7- and 4-alkyl-1-tosylindoles (**9** and **10**) was accomplished by combination of the Friedel-Crafts acylation of **4**, and the treatment of **7** and **8** with H_2SO_4 in 2-propanol as illustrated in Chart 2. Further a novel synthetic method of **16** was devised from **14** by way of **15**.

An alkylindole having its substituents at the benzene portion of the indole nucleus has become an important class of the structural unit for a variety of biologically active natural products, such as ergot alkaloids,[2] marine alkaloids (hapalindoles[3] and trikentrins[4]), tumor promoters (teleocidins A[5] and teleocidins B[6]), and tremorgenic mycotoxins (paspaline and its congener[7]). Consequently it is urgently needed to elaborate a general procedure for preparing various types of alkylindoles, where alkyl substituents are located at the 4, 5, 6, and/or 7 positions of indole in the form either of a complex branched alkyl side chain or of an alkyl-substituted alicyclic ring condensed to the indole nucleus. We are on the way of such effort and in this paper we describe the applicability of our novel method of alkylindole synthesis reported in Part 2.[1]



Scheme 1

Our previous pathway is composed of two parts: (i) the ready transformation of 2-formyl-1-tosylpyrrole (**1**) into variously substituted 1-tosyl-2-pyrrolylcarbinol derivatives (**2**), and (ii) the H_2SO_4-catalyzed cyclization reaction of **2** in refluxing 2-propanol to yield 1-tosylindoles (**3**) (Scheme 1). To improve this procedure, other variants for the first part are conceivable on the basis of the literatures stating that the Friedel-Crafts reaction on 1-phenylsulfonylpyrrole affords 2-acyl derivatives by use of $BF_3{\cdot}Et_2O$, while 3-acyl derivatives are major products using $AlCl_3$ as a catalyst.[8–10] Application of these facts to our pathway led us to furnish a three-step synthesis of 4- and 7-alkylindoles (**10** and **9**) as follows (Scheme 2).



R = **a** : Me; **b** : Cyclohexyl; **c** : 2-Ethoxycarbonylethyl; **d** : 1-Naphthyl

Scheme 2

1-Tosylpyrrole (**4**) was converted to 2- and 3-acetyl- (**5a** and **6a**), cyclohexanoyl- (**5b** and **6b**), 3-ethoxycarbonylpropanoyl- (**5c** and **6c**), and 3-(1-naphthoyl)- (**6d**) pyrroles as shown in Table 1 by selecting combination of the acylating agents and Lewis acid catalysts. Regioselectivity was fairly good except for the formation of 2-cyclohexanoylpyrrole (**5b**) of Entry 3. The Grignard reaction on these acylpyrroles (**5** and **6**) with 2-(1,3-dioxolan-2-yl)ethylmagnesium bromide provided the corresponding tertiary alcohols (**7** and **8**) in very good yields. In cases of Entries 5 and 6, γ-lactone derivatives (*e .g.*, **7c** = **13**) were the sole products. Indole cyclization reaction proceeded readily by refluxing **7** or **8** in 6% sulfuric acid containing 2-propanol for 0.25 – 1 h. 1-Tosylindoles (**10** or **9**) having the substituents at 4- or

7-position were produced in 66 – 82% yields. The lactone ring was opened during the indole synthesis and 2-propyl esters of 3-(1-tosyl-7- and 4-indolyl)prpionic acids (**9c** and **10c**) were obtained in Entries 5 and 6. The tosyl group was easily removed as reported previously either with Mg in methanol[1] in the case of **10b** to afford **12b** in 96% yield, or by alkaline hydrolysis of **10c** and **10d** with 10% KOH in DME-MeOH-H_2O (2:1:1) to give methyl 3-(4-indolyl)propionate (**12c**) (after work-up with diazomethane) and **12d** in 89% and 93% yields.

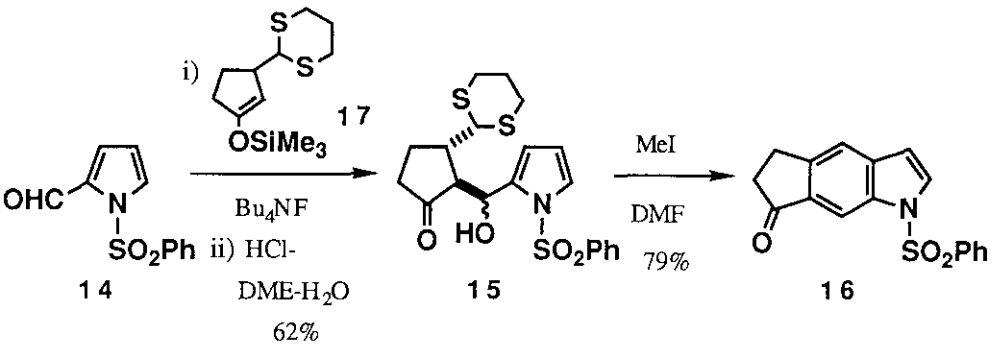
Table 1 Friedel-Crafts Acylation of 1-Tosylpyrrole (**4**) and Subsequent Formation of 4- and 7-Alkyl-1-tosylindoles (**10** and **9**)

Entry			Acylation of **4**			Grignard Reaction		Indole Synthesis		
	R	X	Reagent[a]		Yield %		Yield %		Reaction Time h	Yield %	
					5	**6**	**7**	**8**		**9**	**10**
1	Me	OAc	A	**a**	83	8	97		0.25	75[b]	
2	Me	OAc	B	**a**	7	90		95	0.25		77
3		Cl	A	**b**	38	51	86		1	69	
4		Cl	B	**b**	0	97		97	0.5		82
5	EtO_2C	Cl	A	**c**	80	10	68[c]		1	76[d]	
6	EtO_2C	Cl	B	**c**	16	79		61[c]	0.5		73[d]
7		Cl	B	**d**	1.5	95		84	1		66

a. A: BF_3·OEt_2. B: $AlCl_3$. b. Lit. 1. c. γ- Lactone derivative. d. 2-Propyl ester.

In relating to a structural unit of the precursor (**2**), the dithioacetal compound (**15**) was designed as a substrate for the indole cyclization reaction (Scheme 3). At first 1,3-dithiane was added to 2-cyclopentenone in a conjugate manner,[11] and the resulting enolate was trapped with chlorotrimethylsilane to yield **17**. This was condensed with 1-phenylsulfonyl-2-formylpyrrole (**14**) using tetrabutylammonium fluoride as a reagent[12] to afford a silyloxy derivative, which was hydrolyzed with an acid to form **15** in 62% yield, calculated from **14**. Indole cyclization of **15** and its *S*-oxide was attempted in several ways with the

unsatisfactory results and finally it was found that simple warming of **15** with MeI in DMF was the best procedure to afford a model compound (**16**) for a synthesis of janthitrem G[7] in 79% yield. This experiment suggested that a novel type of alkylindoles such as **16** can be generally synthesized from three components, *i.e.*, an enone, dithiane, and the pyrrole derivative (**14**).



Scheme 3

In the next paper,[13] we describe further examples of application of our H_2SO_4 – 2-propanol method for the indole synthesis.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-melting point apparatus and are not corrected. Mass spectra were taken on Hitachi RMS-4 spectrometer. Ir absorption spectra were determined on Hitachi 215 spectrophotometer. Nmr spectra were measured at Varian EM 390 spectrometer. Column chromatography was conducted on silica gel, Fuji Davison BW 200 and preparative thin-layer chromatography (ptlc) was carried out on glass plates (20×20 cm) coated with Merck silica gel 60 PF_{254} (1 mm thick). Usual work-up refers to washing the organic layers with water or brine, drying on anhydrous sodium sulfate and evaporation of the solvents under reduced pressure.

2-Acetyl-1-tosylpyrrole (5a) — The Friedel-Crafts reaction on 1-tosylpyrrole (**4**) was carried out according to the literature[9] concerning to the reaction on 1-phenylsulfonylpyrrole. Colorless prisms, mp 106-107°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32. Found: C, 59.21; H, 5.06; N, 5.29. Ms *m/z*: 263 (M^+). Ir (KBr) cm^{-1}: 1672. Nmr ($CDCl_3$) δ: 2.33 (3H, s), 2.38 (3H, s), 6.30 (1H, dd, J=3.5, 3.5 Hz), 7.02 (1H, dd, J=3.5, 1.5 Hz), 7.28 and 7.88 (A_2B_2, J=8.5 Hz), 7.79 (1H, dd, J=3.5, 1.5 Hz).

3-Acetyl-1-tosylpyrrole (6a) — Colorless needles, mp 89-90°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32. Found: C, 59.11; H, 4.92; N, 5.26. Ms *m/z*: 263 (M^+). Ir

(KBr) cm^{-1}: 1660. Nmr ($CDCl_3$) δ: 2.37 (3H, s), 2.40 (3H, s), 6.67 (1H, dd, J=3, 1.5 Hz), 7.14 (1H, dd, J=3, 3 Hz), 7.34 and 7.82 (A_2B_2, J=8.5 Hz), 7.70-7.82 (1H, m).

2-Cyclohexanoyl-1-tosylpyrrole (5b) — Colorless syrup. Ms *m/z*: 331 (M^+). Ir ($CHCl_3$) cm^{-1}: 1670. Nmr ($CDCl_3$) δ: 2.34 (3H, s), 2.63-3.02 (1H, m), 6.26 (1H, dd, J=3.5, 3.5 Hz), 6.96 (1H, dd, J=3.5, 1.5 Hz), 7.24 and 7.86 (A_2B_2, J=8.5 Hz), 7.71 (1H, dd, J=3.5, 1.5 Hz).

3-Cyclohexanoyl-1-tosylpyrrole (6b) — Colorless prisms, mp 105-106°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{18}H_{21}NO_3S$: C, 65.23; H, 6.39; N, 4.23. Found: C, 65.04; H, 6.49; N, 4.17. Ms *m/z*: 331 (M^+). Ir (KBr) cm^{-1}: 1670. Nmr ($CDCl_3$) δ: 2.39 (3H,s), 2.64-3.01 (1H, m), 6.64 (1H, dd, J=3.5, 1.5 Hz), 7.09 (1H, dd, J=3.5, 2.5 Hz), 7.29 and 7.78 (A_2B_2, J=8.5 Hz), *ca.* 7.63-7.78 (1H, m).

2-(3-Ethoxycarbonylpropanoyl)-1-tosylpyrrole (5c) — Colorless needles, mp 90.5-91.5°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{17}H_{19}NO_5S$: C, 58.44; H, 5.48; N, 4.01. Found: C, 58.34; H, 5.42; N, 3.89. Ms *m/z*: 349 (M^+). Ir (KBr) cm^{-1}: 1730, 1680. Nmr ($CDCl_3$) δ: 1.16, (3H, t, J=7.5 Hz), 2.36 (3H, s), 2.58 (2H, t, J=6.5 Hz), 3.01 (2H, t, J=6.5 Hz), 4.04 (2H, q, J=7.5 Hz), 6.29 (1H, dd, J=3.5, 3.5 Hz), 7.08 (1H, dd, J=3.5, 2 Hz), 7.25 and 7.85 (A_2B_2, J=8.5 Hz), 7.75 (1H, dd, J=3.5, 2 Hz).

3-(3-Ethoxycarbonylpropanoyl)-1-tosylpyrrole (6c) — Colorless syrup. Ms *m/z*: 349 (M^+). Ir (film) cm^{-1}: 1733, 1680. Nmr ($CDCl_3$) δ: 1.23 (3H, t, J=7.5 Hz), 2.41 (3H, s), 2.67 (2H, t, J=6.5 Hz), 3.07 (2H, t, J=6.5 Hz), 4.12 (2H, q, J=7.5 Hz), 6.67 (1H, dd, J=3.5, 1.5 Hz), 7.13 (1H, dd, J=3.5, 2 Hz), 7.31 and 7.78 (A_2B_2, J=8.5 Hz), *ca.* 7.71-7.81 (1H, m).

2-(1-naphthoyl)-1-tosylpyrrole (5d) — Colorless syrup. Ms *m/z*: 375 (M^+). Ir ($CHCl_3$) cm^{-1}: 1648. Nmr ($CDCl_3$) δ: 2.43 (3H, s), 6.22 (1H, dd, J=3.5, 3.5 Hz), 6.51 (1H, dd, J=3.5, 1.5 Hz), *ca.* 7.20-7.66 (4H, m), 7.34 and 8.03 (A_2B_2, J=8.5 Hz), *ca.* 7.73-8.14 (3H, m), 7.82 (1H, dd, J=3.5, 1.5 Hz).

3-(1-naphthoyl)-1-tosylpyrrole (6d) — Colorless syrup. Ms *m/z*: 375 (M^+). Ir ($CHCl_3$) cm^{-1}: 1640. Nmr ($CDCl_3$) δ: 2.38 (3H, s), 6.79 (1H, dd, J=3.5, 1.5 Hz), 7.14 (1H, dd, J=3.5, 2 Hz), 7.24 and 7.71 (A_2B_2, J= 8.5 Hz).

Grignard Reaction on Acylpyrroles (5 and 6) — Preparation of **8b** is shown as a typical example. A solution of **6b** (85 mg) in THF (3 ml) was treated at -20°C for 15 min under Ar atmosphere with the Grignard reagent (0.83 ml), prepared from Mg (90 mg) and 2-(1,3-dioxolan-2-yl)ethyl bromide (0.60 ml) in THF (3.4 ml). The reaction was quenched with sat. NH_4Cl-H_2O, and the mixture was extracted with CH_2Cl_2. Usual work-up and purification by ptlc [hexane-EtOAc (5:2)] yielded **8b** (108 mg, 97%) as colorless syrup. Ms *m/z*:433 (M^+). Nmr ($CDCl_3$) δ: 2.35 (3H, s), 2.59 (1H, br s, OH), 3.62-4.01 (4H, m), 4.75 (1H, dd, J=4, 4 Hz), 6.08 (1H, dd, J=3, 1.5 Hz), 6.92-7.10 (2H, m), 7.19 and 7.66 (A_2B_2, J=8.5 Hz). In the similar way, **7a**,[1] **7b**, **8a**, and **8d** were prepared. For **7c**, the reaction was carried out at -53 – -20°C and for **8c** at -55 – -47°C. **7b**: Colorless syrup. Ms *m/z*: 433 (M^+). Nmr ($CDCl_3$) δ: 2.34 (3H, s), 3.62-4.01 (4H, m), 4.01 (1H, s, OH), 4.72 (1H, dd, J=4.5, 4.5 Hz), 6.10 (1H, dd, J=3.5, 2 Hz), 6.16 (1H, dd, J=3.5, 3.5 Hz), 7.22 and 7.60 (A_2B_2, J=8.5 Hz), 7.28 (1H, dd, J=3.5, 2 Hz). **7c=13**: Colorless syrup. Ms *m/z*: 405 (M^+). Ir ($CHCl_3$) cm^{-1}: 1773. Nmr ($CDCl_3$) δ: 2.34 (3H, s), 3.60-4.03 (4H, m), 4.73 (1H, dd, J=4, 4 Hz), 6.18 (1H, dd, J=3.5, 3.5 Hz), 6.36 (1H, dd, J=3.5, 2 Hz), 7.22 and 7.64 (A_2B_2, J=8.5 Hz), 7.39 (1H, dd, J=3.5, 2 Hz). **8a**: Colorless syrup. Ms *m/z*: 365 (M^+). Nmr ($CDCl_3$) δ: 1.40 (3H, s), *ca.* 1.45-1.96 (4H, m), 2.36 (3H, s), 2.76 (1H, s, OH), 3.64-4.03 (4H, m), 4.79

(1H, dd, J=4, 4 Hz), 6.21 (1H, dd, J=2.5, 2.5 Hz), 7.07 (2H, d, J=2.5 Hz), 7.26 and 7.73 (A_2B_2, J=8 Hz). **8c** (γ-lactone compound): Colorless syrup. Ms *m/z*: 405 (M^+). Ir ($CHCl_3$) cm^{-1}: 1770. Nmr ($CDCl_3$) δ: 2.37 (3H, s), 3.63-4.01 (4H, m), 4.76 (1H, dd, J=4, 4 Hz), 6.19 (1H, dd, J=3, 2 Hz), 7.07-7.20 (2H, m), 7.28 and 7.73 (A_2B_2, J=8.5 Hz). **8d**: Colorless syrup. Ms *m/z*: 477 (M^+). Nmr ($CDCl_3$) δ: 1.17-1.97 (2H, m), 2.16-2.82 (2H, m), 2.33 (3H, s), 3.22 (1H br s, OH), 3.52-3.93 (4H, m), 4.71 (1H, dd, J=4, 4 Hz), 6.04 (1H, dd, J=3.5, 1.5 Hz), 7.13 and 7.54 (A_2B_2, J=8.5 Hz).

Indole Cyclization Reaction — Synthesis of **4-Cyclohexyl-1-tosylindole (10b)** from **8b** is a representative. A solution of **8b** (73 mg) in 6% H_2SO_4 – 2-propanol (4.5 ml) was refluxed for 30 min. After cooling, H_2O was added and the mixture was extracted with CH_2Cl_2. Reported work-up[1] and ptlc [hexane-EtOAc (9:1)] gave **10b** (49 mg, 82%) as colorless syrup. Ms *m/z*: 353 (M^+). Nmr ($CDCl_3$) δ: 2.22 (3H, s), 2.59-3.01 (1H, m), 6.69 (1H, d, J=4 Hz), 7.01 (1H, br d, J=7.5 Hz), 7.10 and 7.71 (A_2B_2, J=8.5 Hz), 7.21 (1H, dd, J=7.5, 7.5 Hz), 7.52 (1H, d, J=4 Hz), 7.79 (1H, br d, J=7.5 Hz). Spectral data of **9a** and **10a** have been already reported.[1]

7-Cyclohexyl-1-tosylindole (9b) — Colorless syrup. Ms *m/z*: 353 (M^+). Nmr ($CDCl_3$) δ: 2.33 (3H, s), 3.27-3.65 (1H, m), 6.62 (1H, d, J=4 Hz), 7.01-7.42 (2H, m), 7.17 and 7.49 (A_2B_2, J=8.5 Hz), 7.74 (1H, d, J=4 Hz).

2-Propyl 3-(1-Tosyl-7-indolyl)propionate (9c) — Colorless syrup. Ms *m/z*: 385 (M^+). Ir ($CHCl_3$) cm^{-1}: 1720. Nmr ($CDCl_3$) δ: 1.17 (6H, d, J=6 Hz), 2.28 (3H, s), 2.43-2.70 (2H, m), 3.20-3.47 (2H, m), 4.97 (1H, qq, J=6, 6 Hz), 6.62 (1H, d, J=4 Hz), *ca.* 6.93-7.24 (2H, m), 7.12 and 7.51 (A_2B_2, J=8.5 Hz), 7.33 (1H, dd, J=6.5, 3 Hz), 7.71 (1H, d, J=4 Hz).

2-Propyl 3-(1-Tosyl-4-indolyl)propionate (10c) — Colorless syrup. Ms *m/z*: 385 (M^+). Ir ($CHCl_3$) cm^{-1}: 1720. Nmr ($CDCl_3$) δ: 1.11 (6H, d, J=6.5 Hz), 2.27 (3H, s), 2.58 (2H, t, J=8 Hz), 3.12 (2H, t, J=8 Hz), 4.94 (1H, qq, J=6.5, 6.5 Hz), 6.70 (1H, d, J=3.5 Hz), 7.02 (1H, d, J=7.5 Hz), *ca.* 7.09-7.34 (1H, m), 7.17 and 7.74 (A_2B_2, J=8.5 Hz), 7.56 (1H, d, J=3.5 Hz), 7.86 (1H, d, J=7.5 Hz).

4-(1-Naphthyl)-1-tosylindole (10d) — Colorless syrup. Ms *m/z*: 397 (M^+). Nmr ($CDCl_3$) δ: 2.31 (3H, s), 6.21 (1H, d, J=4 Hz), 7.19 and 7.78 (A_2B_2, J=8.5 Hz), 7.46 (1H, d, J=4 Hz), 7.68-7.98 (2H, m), 8.04 (1H, br d, J=7.5 Hz).

Synthesis of 4-Cyclohexylindole (12b) by Reductive Deprotection of 10b — Previously reported procedure[1] afforded **12b** as colorless needles, mp 155-156°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.32; H, 8.71; N, 6.95. Ms *m/z*: 199 (M^+). Nmr ($CDCl_3$) δ: 1.03-2.19 (10H, m), 2.73-3.14 (1H, m), 6.57 (1H, dd, J=3, 2 Hz), 6.84-7.22 (4H, m), 7.95 (1H, br s).

Synthesis of Methyl 3-(4-Indolyl)propionate (12c) from 10c — 2-Propyl ester (**10c**) (33 mg) was treated with 10% KOH – DME-MeOH-H_2O (2:1:1) (2 ml) at 50°C for 3 h. After cooling to 0°C, MeOH (2 ml), 10% HCl-H_2O (4.5 ml) and Et_2O solution of CH_2N_2 were added, and the mixture was stirred at 0°C for 15 min. Addition of sat. NH_4Cl-H_2O, extraction with Et_2O, usual work-up, and ptlc [hexane-EtOAc (4:1)] afforded **12c** (15.5 mg, 89%) as colorless oil. Ms *m/z*: 203 (M^+). Ir (film) cm^{-1}: 3410, 1726. Nmr ($CDCl_3$) δ: 2.59-2.88 (2H, m), 3.08-3.38 (2H, m), 3.65 (3H, s), 6.46-6.61 (1H, m), 6.88 (1H, dd, J=6.5, 1.5 Hz), 6.97-7.30 (3H, m), 8.20 (1H, br s).

4-(1-Naphthyl)indole (12d) — A solution of **10d** (56 mg) in 10% KOH – DME-MeOH-H_2O (2:1:1) (4 ml) was stirred at 35°C for 3 h. Addition of sat. NH_4Cl-H_2O, extraction with CH_2Cl_2, usual work-up, and ptlc [hexane-CH_2Cl_2 (2:3)] afforded **12d** (32 mg, 93%) as colorless prisms, mp 201-203°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{18}H_{13}N$: C, 88.85; H, 5.39; N, 5.76. Found: C, 88.70; H, 5.52; N, 5.77. Ms *m/z*: 243 (M^+). Nmr ($CDCl_3$) δ: 6.10-6.24 (1H, m), 7.11 (1H, dd, J=3, 3 Hz), 7.69-8.01 (3H, m), 8.19 (1H, br s).

2-Formyl-1-phenylsulfonylpyrrole (14) — Employing the procedure for preparation of 2-formyl-1-tosylpyrrole,[1] a solution of 2-formylpyrrole (2.480 g) in CH_2Cl_2 (20 ml) was treated with benzenesulfonyl chloride (4.0 ml) in the presence of Et_3N (8 ml) and 4-dimethylaminopyridine (50 mg) to give **14** (5.276 g, 86%) as colorless needles, mp 81-82°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{11}H_9NO_3S$: C, 56.16; H, 3.86; N, 5.96. Found: C, 56.10; H, 3.97; N, 5.90. Ms *m/z*: 235 (M^+). Ir (KBr) cm^{-1}: 1655. Nmr ($CDCl_3$) δ: 6.93 (1H, dd, J=3.5, 3.5 Hz), 7.14 (1H, dd, J=3.5, 1.5 Hz), 7.36-7.76 (3H, m), 7.76-8.06 (2H, m), 9.93 (1H, s).

3-(1,3-Dithian-2-yl)-1-trimethylsilyloxycyclopentene (17) — A solution of dithiane (247 mg) in THF (4 ml) was treated with 15% BuLi in hexane (1.32 ml) under Ar atmosphere at -80°C for 5 min and at -20°C for 1 h. It was cooled again to -80°C, HMPA (1.20 ml) was added to this, and the mixture was stirred at -80°C for 7 min. A solution of 2-cyclopentenone (161 mg) in THF (2 ml) was further added dropwise and the whole was stirred at -79 – -66°C for 1 h and quenched with chlorotrimethylsilane (0.87 ml) at -79°C. After stirring at -79 – -75°C for 15 min, Et_3N (1.36 ml) was added at -75°C, the mixture was poured into sat. $NaHCO_3$-H_2O, and extracted with Et_2O. The organic layer was washed successively with brine, 0.1*N* citric acid-H_2O, sat. $NaHCO_3$-H_2O, and brine, dried over anhyd. Na_2SO_4, and evaporated in reduced presure to leave crude **17** (528 mg), which was used without further purification. Nmr ($CDCl_3$) δ: 0.23 (9H, s), 3.99 (1H, d, J=6.5 Hz), 4.64 (1H, br s).

The Compound (15) — To a solution of **14** (110 mg) and **17** (528 mg) obtained above in THF (5 ml) was added 1.0 *M* Bu_4NF in THF (0.08 ml) under Ar atmosphere at -70°C, and the mixture was stirred at -70 – -62°C for 50 min. Addition of sat. NH_4Cl-H_2O, extraction with Et_2O, and usual work-up gave a residue (577 mg). This was dissolved in DME (9 ml) and treated with 10% HCl-H_2O (1 ml) at 0°C for 15 min and at room temperature for 2 h. Addition of sat. $NaHCO_3$-H_2O at 0°C, extraction with CH_2Cl_2, usual work-up, and ptlc [benzene-EtOAc (5:1)] afforded **15** (127 mg, 62%), colorless prisms, mp 171-173°C (CH_2Cl_2-MeOH). Anal. Calcd for $C_{20}H_{23}NO_4S_3$: C, 54.89; H, 5.30; N, 3.20. Found: C, 54.59; H, 5.28; N, 3.16. Ms *m/z*: 437 (M^+). Ir (KBr) cm^{-1}: 3430, 1732. Nmr ($CDCl_3$) δ: 3.17 (1H, dd, J=8.5, 3.5 Hz), 3.63 (1H, d, J=4 Hz), 5.60 (1H, br dd, J=4.5, 3.5 Hz), 6.29 (1H, dd, J=3.5, 3.5 Hz), 6.36-6.50 (1H, m), 7.32 (1H, dd, J=3.5, 2 Hz), 7.38-7.73 (3H, m), 7.73-7.96 (2H, m).

1-Phenylsulfonyl-1,5-dihydrocyclopent[*f*]indol-7(6*H*)-one (16) — A solution of **15** (48 mg) and MeI (0.5 ml) in DMF (2 ml) was warmed at 45°C for 57 h. Sat. $NaHCO_3$-H_2O was added to its ice-cooled mixture, which was extracted with Et_2O. Usual work-up and ptlc [hexane-CH_2Cl_2 (3:1)] afforded **16** (27 mg, 79%), colorless needles, mp 220-221°C (CH_2Cl_2-MeOH). Anal. Calcd for $C_{17}H_{13}NO_3S$: C, 65.58; H, 4.21; N, 4.50. Found: C, 65.35; H, 4.40; N, 4.52. Ms *m/z*: 311 (M^+). Ir (KBr) cm^{-1}: 1702, 1685, 1613. Nmr ($CDCl_3$) δ: 2.60-2.84 (2H, m), 3.01-3.28 (2H, m), 6.63 (1H, d, J=4 Hz), 7.23-7.63 (3H, m), 7.50 (1H, s), 7.71 (1H, d, J=4 Hz), 7.78-7.99 (2H, m), 8.33 (1H, s).

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