Synthesis of an Indole Analog of Magallanesine *via* the [1,2]-Meisenheimer Rearrangement

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Ring expansion of azetopyridoindole **11** *via* the [1,2]-Meisenheimer rearrangement of the corresponding *N*-oxide **12** gave azocinoindole **14**, which was converted into the *N*-benzoylenaminone **18** in 5 steps. Intramolecular cyclization of **18** was accomplished by a modified Heck reaction followed by reductive desulfonylation to provide the indole analog **2**, 5*H*-isoindolo[2',1';1,2]azocino[5,6-*b*]indole, of magallanesine **1**.

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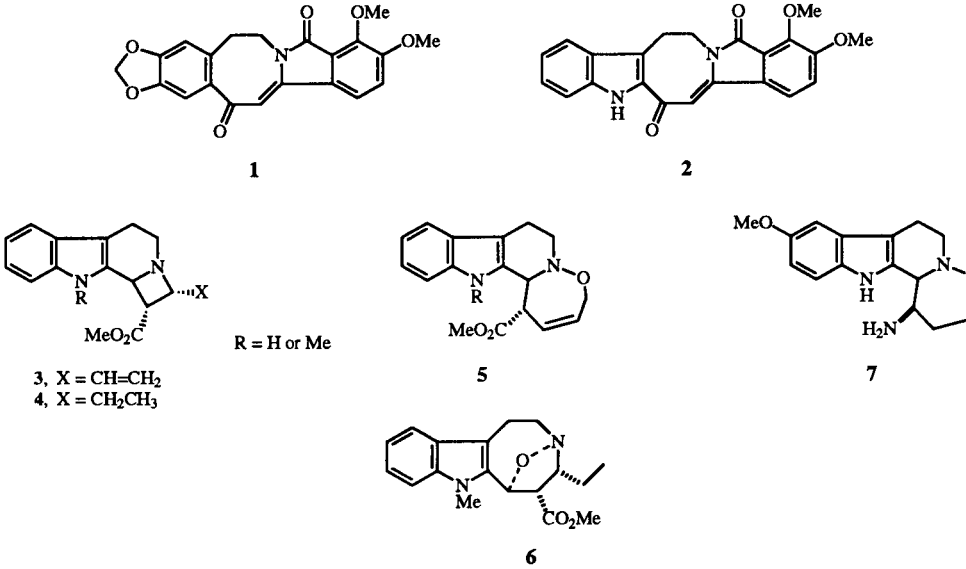
Introduction.

Medium membered nitrogen heterocycles [1,2] have become increasingly important in organic chemistry, owing to their diverse and significant biological activities. As the medium membered rings are generally much more difficult to prepare by the cyclization of acyclic precursors, the ring-opening strategy is widely noticed for the synthesis [2,3]. During the course of our extensive works upon the Meisenheimer rearrangements of hexahydroazeto[1',2':1,2]-pyrido[3,4-*b*]indole *N*-oxides, we found two different modes of the ring expansion of the azetopyridoindoles **3** and **4**: the former resulted in an oxazepinopyridoindole **5** [4,5] *via* the [2,3]-rearrangement of the *N*-oxide generated *in situ*, while the latter an epoxyazocinoindole **6** [6] *via* the [1,2]-rearrangement of the corresponding *N*-oxide, respectively. We recently attained the synthesis of (±)-12-carbaeudistomin **7** [7] by using the [2,3]-Meisenheimer rearrangement as the key reaction. Interestingly, the antivial activities of **7** against influenza virus revealed the same extent of activities as those of natural (-)-debromoeudistomin K. Further, easy reductive cleavage of the epoxy ring of the product **6** [6] provided a concise method for the synthesis of hexahydroazocino[5,6-*b*]indoles. The utility of this methodology was demonstrated by the total synthesis of magallanesine **1** [8], a new class of isoindolobenzazocine alkaloid isolated from *Berberis darwinii* [9]. Since magallanesine itself, however, does not possess any useful pharmacological activities, we were naturally interested in a modified structure of **1**, in which the methylenedioxybenzene ring was replaced by an indole ring. In an effort to expand the scope of our methodology, we herein describe the synthesis of the indole analog **2**, isoindolo[2',1';1,2]azocino[5,6-*b*]indole, of magallanesine **1** aimed at evaluating the biological activities.

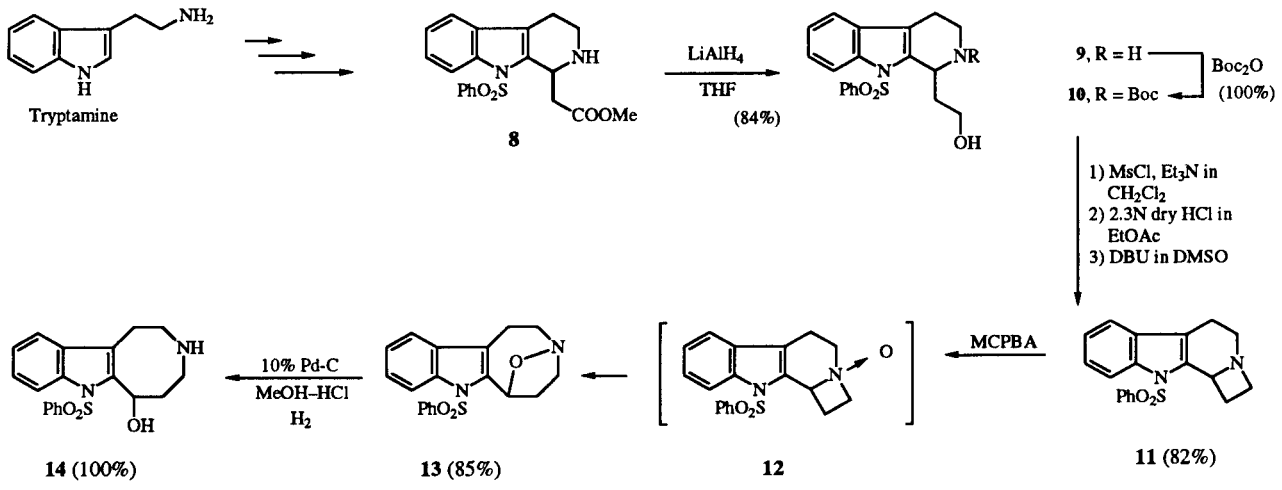
Results and Discussions.

We first explored preparation of the azetopyridoindole **11**, having a benzenesulfonyl group as a protective group of the indole nitrogen atom, which is a critical intermediate for the synthesis of **2** (Scheme 1). Reduction of the

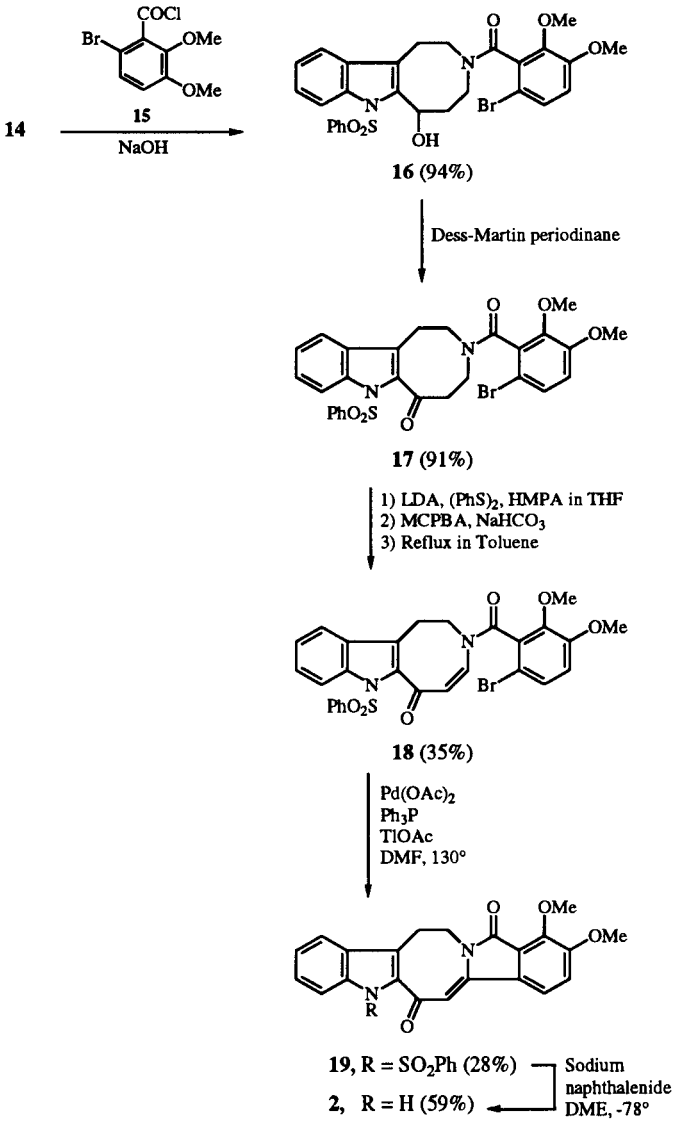
Figure



Scheme 1



Scheme 2



carbolineacetate **8**, prepared from tryptamine [5], with lithium aluminun hydride in tetrahydrofuran gave an alcohol **9** (84%), whose amino function was protected by a *tert*-butoxycarbonyl (Boc) group to yield a carbamate **10**. Conversion of the compound **10** into the azetidine **11** could be done in 82% overall yield by successive treatments [10] with i) methanesulfonyl chloride and triethylamine, ii) dry hydrogen chloride, and iii) 1,8-diazabicyclo[5.4.0]undec-7-ene in dichloromethane. Assignment of the structure of **11** was made on the bases of mass [m/z (338 M^+)], ^1H nmr (δ 5.05, dd, 10b-H) and ^{13}C nmr (δ 57.47, 10b-C) spectra. Compound **11** was then reacted with *m*-chloroperbenzoic acid in dichloromethane at -23° ~ -26° to give an *N*-oxide **12**. Without isolation, it was heated at 40° for 15 minutes to afford an epoxyazocinoindole **13** (85%). Hydrogen peroxide oxidation of **11** also gave the compound **13** (85%), but longer reaction times were required for consumption of **11**. The mass spectrum [m/z 354 (M^+)] of **13** indicated the insertion of one oxygen atom to **11**, *via* the [1,2]-Meisenheimer rearrangement of **12** formed *in situ*. Reductive cleavage of the N-O bond of **13** over 10% palladium carbon afforded an amino alcohol **14** in quantitative yield (Scheme 2). Schotten-Baumann condensation with benzoyl chloride **15**, prepared by treatment of the known carboxylic acid [11] with thionyl chloride, afforded an amide **16** in 94% yield. Although the ^1H nmr spectrum of **16** was not sufficiently resolved to complete the assignment of the structure due to the inseparable mixture of rotational isomers, elemental analysis and ir spectrum supported its structure. Oxidation of **16** with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess-Martin periodinane) [12] gave the ketone **17** in 91% yield in dichloromethane at room temperature. Phenylsulfenylation (lithium diisopropylamide and diphenyl disulfide) and *m*-chloroperbenzoic acid oxidation followed by thermolysis of the resulting sulfoxide in toluene gave an enaminone **18** in 35% overall yield.

Cyclization to isoindoloazocinoindole skeleton was carried out by using the modified Heck reaction [13]. Heating of **18** with palladium (II) acetate in the presence of thallium (I) acetate and triphehyl phosphine gave 5,14-dioxo-5*H*-isoindoloazocinoindole **19** in 28% yield in dimethylformamide at 130°. The structure of **19** was verified on the bases of elemental analysis and spectroscopic data [ir: 1720 and 1640 (CO) cm^{-1}, and ^1H nmr: δ 6.40 (s, 1H, 15-H)]. Although the reductive debenzenesulfonylation under various conditions such as magnesium in methanol [5] or samarium (II) iodide [14] did not give satisfactory results, the target compound **2** could be successfully obtained by reduction of **19** with sodium naphthalenide in dimethoxyethane at -78° in 59% yield. Biological evaluations of **2** are in progress.

EXPERIMENTAL

General.

Melting points were determined using a Yanagimoto micromelting point apparatus and are uncorrected. The ir were recorded on a Shimadzu IR-435 spectrometer. The ^1H and ^{13}C nmr were obtained in deuteriochloroform, unless otherwise stated, with a Varian Gemini-200 spectrometer; signals are given in ppm. Low-resolution and high-resolution mass (hrms) spectra were obtained on a Hitachi M-4000H instrument. The C, H, N elemental analyses were performed on a Yanako CHN CORDER MT-3. For column chromatography, silicagel (Merck 7734 or 9385) was used.

9-Benzenesulfonyl-1,2,3,4-tetrahydro-β-carboline-1-ethanol (**9**).

A solution of **8** (5.53 g, 14.4 mmoles) in tetrahydrofuran (40 ml) was added to a suspension of lithium aluminum hydride (2.19 g, 57.6 mmoles) in tetrahydrofuran (20 ml) under ice-cooling. After being stirred for 5 minutes, the reaction was quenched by dropwise addition of water (5 ml) and diluted with dichloromethane (200 ml). The reaction mixture was dried with magnesium sulfate and filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography [chloroform-methanol (20:1)] to give **9** (4.30 g, 84%) as crystals, mp 183-186° (from a mixture of ethanol and hexane); ir (potassium bromide): 3500-2800 (NH, OH), 1370 and 1170 (SO_2) cm^{-1}; ^1H nmr: δ 1.97-2.35 (m, 2H, CH_2CH_2OH), 2.48-2.87 (m, 2H, C4-H_2), 3.18 (dd, J = 8.8, 4.4 Hz, 2H, C3-H_2), 3.87 (td, J = 11.1, 3.8 Hz, 1H, CH_2CHHOH), 4.09 (td, J = 11.1, 2.7 Hz, 1H, CH_2CHHOH), 4.70 (br d, J = 12.3 Hz, 1H, C1-H), 7.20-7.70 (m, 8H, ArH), 8.12 (d, J = 7.5 Hz, 1H, C8-H); ms: m/z 356 (M^+).

Anal. Calcd. for $C_{19}H_{20}N_2O_3S$: C, 64.02; H, 5.66; N, 7.86. Found: C, 64.14; H, 5.62; N, 7.67.

9-Benzenesulfonyl-2-*tert*-butoxycarbonyl-1,2,3,4-tetrahydro-β-carboline-1-ethanol (**10**).

A solution of di-*tert*-butyldicarbonate (2.70 g, 12.4 mmoles) in tetrahydrofuran (20 ml) was added dropwise to a solution of **9** (4.19 g, 11.8 mmoles) in tetrahydrofuran (80 ml) at room temperature and the mixture was allowed to stand for 1 hour. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography [chloroform-ethyl acetate (10:1)] to give **10** (5.40 g, 100%) as crystals, mp 160-161° (from a mixture of ethanol and hexane); ir (potassium bromide): 1670 (CO), 1170 and 1370 (SO_2) cm^{-1}; ^1H nmr: δ 1.51 (s, 9H, $COOCMe_3$), 1.75-2.04 (m, 2H, CH_2CH_2OH), 2.48-2.85 (m, 2H, C4-H_2), 3.10 (m, 1H, C3-H), 3.65-3.93 (m, 2H, CH_2OH), 4.16-4.54 (m, 1H, C3-H), 6.03 (m, 1H, C1-H), 7.18-7.84 (m, 8H, ArH), 8.18 (d, J = 7.5 Hz, 1H, C8-H); ms: m/z 456 (M^+).

Anal. Calcd. for $C_{24}H_{28}N_2O_5S \cdot 1/10H_2O$: C, 62.64; H, 6.18; N, 6.09. Found: C, 62.67; H, 6.05; N, 6.07.

10-Benzenesulfonyl-1,2,4,5,10,10b-hexahydroazeto[1',2';1,2]-pyrido[3,4-*b*]indole (**11**).

Triethylamine (1.04 ml, 7.43 mmoles) and methanesulfoyl chloride (0.57 ml, 7.43 mmoles) were added successively to a solution of **10** (3.08 g, 6.75 mmoles) in dichloromethane (10 ml) under ice-cooling, and the mixture was stirred at room temperature for 10 minutes. The reaction was quenched with water, and extracted with dichloromethane. The extract was washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was, without purification, dissolved in 2.3*N* hydrogen chloride in ethyl acetate (20 ml) and the solution was stirred for 1 hour at room temperature. After removal of the solvent *in vacuo*, the residue was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (2.43 ml, 16.2 mmoles) in dichloromethane (20 ml), and the mixture was stirred at room temperature for 10 hours. The reaction mixture was then diluted with dichloromethane (20 ml). The solution was washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography [chloroform-methanol (50:1)] to give **11** (1.86 g, 82%) as crystals, mp 155-157° (from ethyl acetate); ir (potassium bromide): 1365 and 1175 (SO_2) cm^{-1}; ^1H nmr: δ 2.02 (m, 1H, C1-H), 2.52-2.73 (m, 2H, C4- and C5-H), 2.80-3.09 (m, 3H, C1-, C4-, and C5-H), 3.26-3.47 (m, 2H, C2-H_2), 5.05 (dd, J = 1.4, 8.1 Hz, 1H, C10b-H), 7.23-7.56 (m, 6H, ArH), 7.78 (d, J = 7.0 Hz, 2H, ArH), 8.15 (d, J = 7.0 Hz, 1H, C9-H); selected ^{13}C nmr: δ 16.5 (5-C), 27.9 (1-C), 42.7 (4-C), 46.8 (2-C), 57.5 (10b-C); ms: m/z 338 (M^+).

Anal. Calcd. for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.45; H, 5.38; N, 8.22.

7-Benzenesulfonyl-3,6-epoxy-1,2,3,4,5,6-hexahydroazocino[5,4-*b*]indole (**13**).

A solution of 80% *m*-chloroperbenzoic acid (318 mg, 1.48 mmoles) in dichloromethane (5 ml) was added to a solution of **11** (500 mg, 1.48 mmoles) in dichloromethane (5 ml) at -23 ~ -26°, and the solution was stirred for 30 minutes. The solution was washed with 5% sodium carbonate solution, water and dried over sodium sulfate. After removal of sodium sulfate by filtration, the filtrate was heated at 40° for 15 minutes, and concentrated *in vacuo*. The residue was purified by column chromatography [chloroform-methanol (50:1)] to give **13** (447 mg, 85%) as crystals, mp 163-164° (from ethanol); ir (potassium bromide): 1375 and 1175 (SO_2) cm^{-1}; ^1H nmr: δ 2.49 (m, 1H, C5-H), 2.73-3.05 (m, 4H, C1-H_2, C2-H, C5-H), 3.35 (m, 2H, C4-H_2), 3.70 (m, 1H, C2-H), 6.05 (dd, J = 3.5, 9.0 Hz, 1H, C6-H), 7.20-7.59 (m, 6H, ArH), 7.80 (d, J = 7.0 Hz, 2H, ArH), 8.14 (d, J = 7.0 Hz, 1H, C8-H); ms: m/z 354 (M^+).

Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.39; H, 5.12; N, 7.90. Found: C, 64.40; H, 5.23; N, 7.86.

7-Benzenesulfonyl-6-hydroxy-1,2,3,4,5,6-hexahydroazocino[5,4-*b*]indole Hydrochloride (**14**).

A solution of **13** (1.84 g, 5.2 mmoles) in methanol (30 ml) containing concentrated hydrochloric acid (0.5 ml) was hydrogenated under the initial pressure of 2 kg/cm^2 with 10% palladium on carbon (185 mg) for 6 hours. After removal of the catalyst by filtration through a Celite pad, the filtrate was concentrated *in vacuo* to give the pure **14** (2.04 g, 100%) as a solid. This was purified by recrystallization from ethanol to give an analytical sample, mp 146-148°; ir (potassium bromide): 3600-2400 (NH, OH), 1370 and 1170 (SO_2) cm^{-1}; ^{1}H nmr (deuteriomethanol): δ 2.18-2.57 (m, 2H, C5-H_2), 3.05-4.0 (m, 6H, C1-, C2-, and C4-H_2), 6.10 (m, 1H, C6-H), 7.27-7.75 and 7.88-8.0 (m, 8H, ArH), 8.22 (d, J = 7.5 Hz, 1H, C8-H); ms: m/z 365 (M$^+$-HCl).

Anal. Calcd. for $C_{19}H_{21}ClN_2O_3S\cdot H_2O$: C, 55.54; H, 5.64; N, 6.82. Found: C, 55.77; H, 5.64; N, 6.83.

7-Benzenesulfonyl-3-(6-bromo-2,3-dimethoxy-1-carbamoyl)-6-hydroxy-1,2,3,4,5,6-hexahydroazocino[5,4-*b*]indole (**16**).

A suspension of 6-bromo-2,3-dimethoxybenzoic acid (1.43 g, 5.5 mmoles) and thionyl chloride (0.79 ml, 11 mmoles) in benzene (30 ml) was refluxed for 6 hours. After removal of the solvent and excess thionyl chloride by evaporation *in vacuo*, the resulting 6-bromo-2,3-dimethoxybenzoyl chloride **15** was dissolved in dimethoxyethane (10 ml). This solution was added to a solution of **14** (2.04 g, 5.2 mmoles) in dimethoxyethane (70 ml) containing a 10% sodium hydroxide solution (6 ml), and the whole was stirred for 5 minutes. The reaction mixture was then diluted with dichloromethane (50 ml). The solution was washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography [chloroform-methanol (50:1)] to give **16** (2.91 g, 94%) as crystals, mp 132-134° (from ethanol); ir (nujol): 3600-3200 (OH), 1630 (C=O), 1370 and 1170 (SO_2) cm^{-1}; ms: m/z 598 (M$^+$).

Anal. Calcd. for $C_{28}H_{27}BrN_2O_6S$: C, 56.10; H, 4.54; N, 4.67 Found: C, 55.94; H, 4.58; N, 4.62.

7-Benzenesulfonyl-3-(6-bromo-2,3-dimethoxybenzene-1-carbamoyl)-6-oxo-1,2,3,4,5,6-hexahydroazocino[5,4-*b*]indole (**17**).

1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess Martin periodinane) (2.034 g, 4.8 mmoles) was added to a solution of **16** (960 mg, 1.6 mmoles) in dichloromethane (20 ml). After being stirred for 15 minutes, the reaction was quenched with 5% sodium hydroxide solution (10 ml). The whole was stirred for 15 minutes, and extracted with dichloromethane. The extract was washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography [benzene-ethyl acetate (10:1)] to give **17** (840 mg, 91%) as crystals, mp 195-197° (from ethanol); ir (potassium bromide): 1700 (C=O), 1645 (CON), 1370 and 1180 (SO_2) cm^{-1}; ^{1}H nmr: δ 2.82-3.68 (m, 6H, C1-, C2-, and C5-H_2), 3.83 and 3.87 (each s, each 3H, MeO x 2), 3.90-4.14 (m, 2H, C4-H_2), 6.80 (d, J = 8.5 Hz, 1H, C4'-H), 7.20-7.62 (m, 7H, ArH), 8.04 (m, 3H, ArH); ms: m/z 596 (M$^+$).

Anal. Calcd. for $C_{28}H_{25}BrN_2O_6S$: C, 56.29; H, 4.22; N, 4.69. Found: C, 56.04; H, 4.18; N, 4.69.

7-Benzenesulfonyl-3-(6-bromo-2,3-dimethoxy-1-carbamoyl)-6-oxo-1,2,3,6-tetrahydroazocino[5,4-*b*]indole (**18**).

A solution of **17** (119 mg, 0.2 mmole) in a mixture of tetrahydrofuran (3 ml) and hexamethylphosphoramide (2 ml) was added dropwise to a solution of lithium diisopropylamide [prepared from diisopropylamine (0.07 ml, 0.5 mmole) and *n*-butyllithium (15% *n*-hexane solution, 0.32 ml, 0.5 mmole)] at -78°, and the mixture was stirred for 1 hour. To this mixture was added diphenyl disulfide (109 mg, 0.5 mmole) at this temperature. After being warmed to room temperature gradually, the mixture was stirred for 2 hours. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The extract was washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. To a solution of the residue dissolved in dichloromethane (5 ml) was added sodium hydrogen carbonate (20 mg, 0.2 mmole) and 80% *m*-chloroperbenzoic acid (34 mg, 0.2 mmole) successively at room temperature. After being stirred for 20 minutes, the reaction mixture was diluted with dichloromethane. The organic layer was washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was dissolved in toluene (5 ml), and the solution was refluxed for 3 hours. After evaporation of the solvent *in vacuo*, the residue was purified by column chromatography [benzene-ethyl acetate (20:1)] to give **18** (42 mg, 35%) as an oil; ir (film): 1680 (C=O), 1655 (CON), 1370 and 1170 (SO_2) cm^{-1}; ^{1}H nmr: δ 3.36 (t, J = 5.6 Hz, 2H, C1-H_2), 3.57 and 3.85 (each s, each 3H, MeO x 2), 4.23 (t, J = 5.6 Hz, 2H, C2-H_2), 5.77 (d, J = 9.1 Hz, 1H, C5-H), 6.86 (d, J = 8.5 Hz, 1H, C4'-H), 6.88 (d, J = 9.1 Hz, 1H, C4-H), 7.21-7.59 (m, 7H, ArH), 7.93-8.04 (m, 3H, ArH); ms: m/z 594 (M$^+$); hrms Calcd. for $C_{28}H_{23}BrN_2O_6S$: 594.0459. Found: 594.0455.

13-Benzensulfonyl-5,14-dioxo-7,8,13,14-tetrahydro-5*H*-isoindolo[2',1';1,2]azocino[5,6-*b*]indole (**19**).

A solution of **18** (45 mg, 0.076 mmole), palladium (II) acetate (4.5 mg, 0.02 mmole), triphenyl phosphine (10 mg, 0.04 mmole) and thallium (I) acetate (21 mg, 0.08 mmole) in dimethylformamide (2 ml) was stirred at 130° for 2 days. After cooling, the mixture was diluted with water (2 ml) and ethyl acetate (20 ml). The organic layer was washed with water and brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography [benzene-ethyl acetate (5:1)] to give **19** (11 mg, 28%) as amorphous powder; ir (potassium bromide): 1720 (C=O), 1640 (CON), 1370 and 1170 (SO_2) cm^{-1}; ^{1}H nmr: δ 3.25 (t, J = 5.0 Hz, 2H, C8-H_2), 3.95 and 4.12 (each s, each 3H, MeO x 2), 4.18 (t, J = 5.0 Hz, 2H, C7-H_2), 6.40 (s, 1H, C15-H), 7.36 (d, J = 8.4 Hz, 1H, C2-H), 7.24-7.58 (m, 7H, ArH), 8.04 (m, 3H, ArH); ms: m/z 514 (M$^+$); hrms Calcd. for $C_{28}H_{22}N_2O_6S$: 514.1197. Found: 514.1198.

5,14-Dioxo-7,8,13,14-tetrahydro-5*H*-isoindolo[2',1';1,2]azocino[5,6-*b*]indole (**2**).

A solution of sodium naphthalenide in dimethoxyethane was prepared by adding dimethoxyethane (50 ml) to a mixture of sodium (500 mg, 22 mmoles) and naphthalene (2.56 g, 20 mmoles) and stirring the resulting mixture at room temperature for 2 hours. A solution of **19** (14 mg, 0.027 mmole) in dimethoxyethane (2 ml) was cooled at -78° and the sodium naphthalenide solution was added dropwise to the stirring sulfonylamide solution until a light green color persisted. The reaction mixture was quenched with water. The resulting solution was extracted with ethyl acetate, and the extract was washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography [benzene-ethyl acetate (5:1)] to give **2** (6 mg, 59%) as crystals, mp 287-292° (from a mixture of ethanol and hexane); ir (potassium bromide): 1730 (C=O), 1620 (CON) cm^{-1}; ^{1}H nmr: δ 3.37 (m, 2H,

C8-H_2), 3.96 and 4.15 (each s, each 3H, MeO x 2), 4.30 (m, 2H, C7-H_2), 6.39 (s, 1H, C15-H), 7.11-7.73 (m, 6H, ArH), 9.26 (br s, 1H, NH); ms: m/z 374 (M^+).

Anal. Calcd. for $C_{22}H_{18}N_2O_4 \cdot 1/5\ H_2O$: C, 69.91; H, 4.91; N, 7.41. Found: C, 70.03; H, 4.83; N, 7.11.

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