sulfate and concentrated to give the product as a dark yellow oil (4.51 g, 96%). The analytical sample was prepared by molecular distillation: bp 105–110 °C (0.05 mmHg); IR (neat) 3390, 1709 cm^{-1}; mass spectrum, m/e 213 (M^+); ^1H NMR ($CDCl_3$) δ 7.80 (br s, 1 H), 7.70 (br s, 1 H, OH, NH), 7.30 (m, 1 H), 7.15 (m, 1 H, both furan H), 4.25 (q, 2 H, CH_2), 1.60 (s, 6 H, CH_3COH), 1.30 (t, 3 H, CH_3CH_2). Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.30; H, 7.09; N, 6.57. Found: C, 55.85; H, 8.13; N, 6.20.

4-(1-Ethyl-1-hydroxypropyl)-3-furancarbamic Acid Ethyl Ester (12b). In a similar manner to the above, ethylmagnesium bromide (0.16 mol) was reacted with 4-carboxy-3-furancarbamic acid diethyl ester (**10**; 7.99 g, 0.035 mol) for 18 h. Upon workup, the product was obtained as a yellow solid (7.60 g, 90%). The analytical sample was prepared from methylene chloride/petroleum ether as buff crystals: mp 70–71 °C; IR (KBr) 3450, 3350, 1700 cm^{-1}; mass spectrum, m/e 241 (M^+); ^1H NMR ($CDCl_3$) δ 7.84 (br s, 2 H, NH, furan H), 6.98 (s, 1 H, furan H), 4.20 (q, 2 H, OCH_2), 1.97 (br s, 1 H, OH), 1.74 (q, 4 H, $C(OH)CH_2$), 1.28 (t, 3 H, CH_3CH_2O), 0.87 (t, 6 H, $CH_3CH_2C(OH)$. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.53; H, 7.95; N, 5.75.

4,4-Dimethyl-4*H*-furo[3,4-*d*][1,3]oxazin-2(1*H*)-one (14a). A mixture of sodium hydride (0.23 g, 0.01 mol) and 4-(1-hydroxy-1-methylethyl)-3-furancarbamic acid ethyl ester (**12a**; 2.13 g, 0.01 mol) was refluxed for 18 h in toluene (50 mL), using a Dean–Stark water separator and 4Å molecular sieves. The reaction mixture was cooled to room temperature and the sodium salt of the product was collected by filtration (1.83 g, 97%). The solid was triturated with methylene chloride (50 mL) and treated with 1 N hydrochloric acid (5 mL) in water (45 mL). The organic layer was separated, dried over sodium sulfate, and concentrated to give the product as a yellow solid (1.55 g, 95% overall). The analytical sample was prepared from methylene chloride/petroleum ether: mp 110.5–112 °C; IR (KBr) 3226, 1680 cm^{-1}; UV (CH_3OH) 205, 217 nm; mass spectrum, m/e 167 (M^+); ^1H NMR (Me_2SO-d_6) δ 9.95 (br s, 1 H, NH), 7.56 (br s, 1 H), 7.24 (br s, 1 H, both furan H), 1.58 (s, 6 H, CH_3). Anal. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.48; N, 8.38. Found: C, 57.46; H, 5.50; N, 8.20.

4,4-Dimethyl-1-methyl-4*H*-furo[3,4-*d*][1,3]oxazin-2-(1*H*)-one (14b). The sodium salt from above (0.38 g, 0.002 mol) was dissolved in dimethylformamide (dry, 5 mL) and treated with methyl iodide (1.42 g, 0.6 mL, 0.01 mol) for 1 h. The mixture was poured into water (25 mL) and the aqueous layer was extracted with methylene chloride (3 × 25 mL). The combined organic layers were concentrated, the residue was triturated with petroleum ether, and the residue was distilled to give the product as a waxy solid (0.27 g, 75%): bp 100 °C (0.05 mmHg); IR (mull) 1705 cm^{-1}; UV (CH_3OH) 203, 216 nm; mass spectrum, m/e 181 (M^+); ^1H NMR ($CDCl_3$) δ 7.15 (d, 1 H), 7.04 (d, 1 H, both furan H), 3.24 (s, 3 H, CH_3N), 1.66 (s, 6 H, CH_3C). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.28; H, 6.12; N, 7.52.

4,4-Diethyl-4*H*-furo[3,4-*d*][1,3]oxazin-2(1*H*)-one (14c). A mixture of 4-(1-ethyl-1-hydroxypropyl)-3-furancarbamic acid ethyl ester (**12b**; 6.72 g, 0.028 mol) and sodium hydride (0.70 g, 0.029 mol) was refluxed in dry toluene (150 mL) as above. The sodium salt (5.96 g, 98.5%) was collected and dried. A sample of the salt (1.25 g, 0.006 mol) was suspended between methylene chloride (50 mL) and 1 N hydrochloric acid (25 mL) for 1 h and worked up as above to give the product as cream crystals (0.85 g, 95%): mp 146–147 °C; IR (KBr) 3280, 1725 cm^{-1}; UV (CH_3OH) 202, 212 nm; mass spectrum, m/e 195 (M^+); ^1H NMR ($CDCl_3$) δ 9.20 (br s, 1 H, NH), 7.16 (br s, 1 H), 7.10 (br s, 1 H, both furan H), 1.88 (q, 4 H, CH_2), 0.96 (t, 6 H, CH_3). Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.36; H, 6.77; N, 7.08.

4,4-Diethyl-1-methyl-4*H*-furo[3,4-*d*][1,3]oxazin-2(1*H*)-one (14d). The sodium salt from above (0.435 g, 0.002 mol) in dry dimethylformamide (5 mL) was treated with methyl iodide (2 mL) and worked up as above to give the product (0.319 g, 76%) which was recrystallized from petroleum ether at −78 °C to give the analytical sample: mp 31–33 °C; IR (KBr) 1709 cm^{-1}; UV (CH_3OH) 203, 216, 270 nm; mass spectrum, m/e 209 (M^+); ^1H NMR ($CDCl_3$) δ 7.08 (m, 2 H, furan H), 3.26 (s, 3 H, NCH_3), 1.86 (q, 4 H, CH_2), 0.94 (t, 6 H, CH_3CH_2). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 61.81; H, 7.31; N, 6.55. Found: C, 61.60; H, 7.11; N, 6.51.

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Registry No. **2**, 78329-55-2; **3**, 34501-80-9; **4**, 78329-56-3; **5**, 78329-57-4; **6a**, 78329-58-5; **6b**, 78329-59-6; **6c**, 78329-60-9; **6d**, 78329-61-0; **6e**, 78329-62-1; **8a**, 78329-63-2; **8b**, 78329-64-3; **10**, 78329-65-4; **11**, 78329-66-5; **12a**, 78329-67-6; **12b**, 78329-68-7; **14a**, 78329-69-8; **14a**·Na, 78329-70-1; **14b**, 78329-71-2; **14c**, 78329-72-3; **14c**·Na, 78329-73-4; **14d**, 78342-36-6; furan-3,4-dicarboxylic acid diethyl ester, 30614-77-8; methylamine, 74-89-5; aniline, 62-53-3; diethylamine·HCl, 660-68-4; phenethylamine, 64-04-0; 4-carboxy-3-furancarbamic acid, 78329-74-5.

Synthesis of Carbazole Alkaloids Hyellazole and 6-Chlorohyellazole[1]

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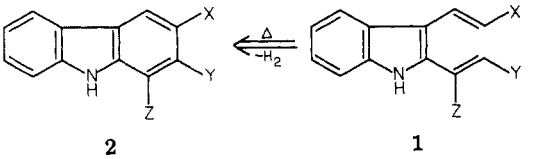
2-(1-Cyclohexenyl)-3-(β-methoxyvinyl)indole was heated in decalin in the presence of 5% Pd–C to give 1,2,3,4-tetrahydro-5-methoxy-11*H*-benzo[*a*]carbazole and 5-methoxy-11*H*-benzo[*a*]carbazole. 3-(β-Methoxyvinyl)-2-(1-phenyl-1-propenyl)indole and 5-chloro-3-(β-methoxyvinyl)-2-(1-phenyl-1-propenyl)indole were also heated in decalin in the presence of 5% Pd–C at 210 °C, yielding the carbazole alkaloids hyellazole and 6-chlorohyellazole, respectively.

We have investigated a new synthetic route to carbazoles by way of thermal cyclization of the triene system (**1**) in the presence of 5% Pd–C, based on the electrocyclic reaction of 1,3,5-trienes providing the cyclohexa-1,3-dienes by either thermal condition or photolysis.[2] Although there

Scheme I



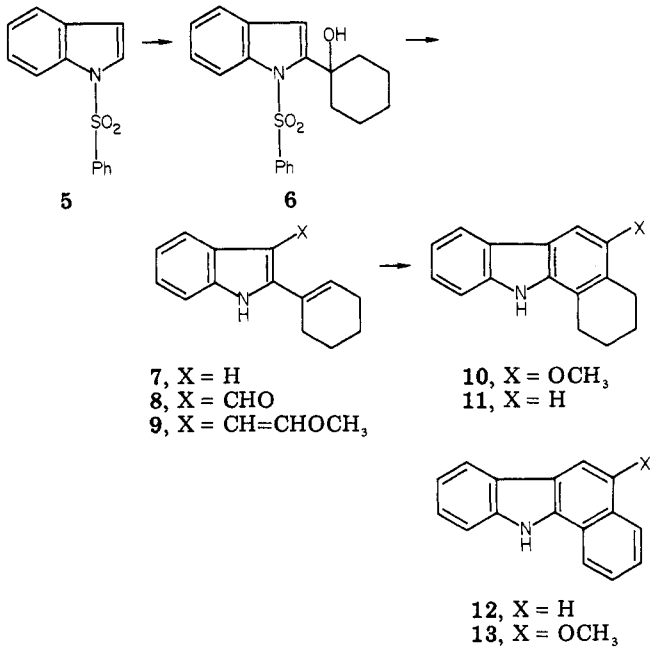
2 **1**

are a number of preparative routes to carbazoles,[3-10] our proposed synthetic method would be useful for preparation

(1) A part of this work was reported in *J. Chem. Soc., Chem. Commun.*, **1980**, 1241, as a preliminary communication.
(2) R. Hoffmann and R. B. Woodward, *Chem. Unserer Zeit*, 6, 167 (1972).

0022-3263/81/1946-3856$01.25/0

Scheme II



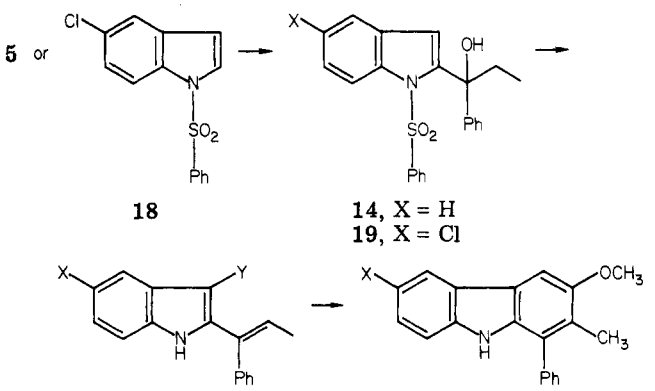
5 6

7, X = H
8, X = CHO
9, X = CH=CHOCH$_3$

10, X = OCH$_3$
11, X = H

12, X = H
13, X = OCH$_3$

Scheme III



18 14, X = H
19, X = Cl

15, X = Y = H
16, X = H; Y = CHO
17, X = H;
Y = CH=CHOCH$_3$
20, X = Cl; Y = H
21, X = Cl;
Y = COCOCl
22, X = Cl;
Y = COCOOEt
23, X = Cl;
Y = COCOOH
24, X = Cl; Y = CHO
25, X = Cl;
Y = CH=CHOCH$_3$

3, X = H
4, X = Cl

of functionalized polysubstituted carbazoles (**2**), since 2,3-divinylindoles can be easily obtained and cyclization intermediates, dihydrocarbazoles, are dehydrogenated to carbazoles with a dehydrogenating agent or catalytically.[11] (See Scheme I.) By this method, carbazole alkaloids hyellazole **3**[1,12] and 6-chlorohyellazole **4**,[12] isolated from the blue-green alga *Hyella caespitosa*, were synthesized. We report the results.

As the model experiment for this purpose, 2-(1-cyclohexenyl)-3-(β-methoxyvinyl)indole (**9**) was prepared, and its thermal cyclization was examined as follows. Condensation of lithio-*N*-(benzenesulfonyl)indole,[13] obtained by LDA treatment of *N*-(benzenesulfonyl)indole (**5**)[13] with cyclohexanone, gave the 2-(1-hydroxycyclohexyl)indole **6**. Hydrolysis of **6** with ethanolic aqueous NaOH resulted in formation of 2-(1-cyclohexenyl)indole **7**, Vilsmeier reaction of which yielded the indole 3-aldehyde **8**. Wittig reaction of **8** with (methoxymethylene)triphenylphosphorane[14] led to the expected 3-(β-methoxyvinyl)indole (**9**), which was heated in xylene in the presence of 5% Pd–C to give 1,2,3,4-tetrahydro-5-methoxy-11*H*-benzo[*a*]carbazole (**10**) and 1,2,3,4-tetrahydro-11*H*-benzo[*a*]carbazole (**11**). When **9** was heated in 1,2-dichlorobenzene at 180 °C, **10** and demethoxylated, fully aromatized 11*H*-benzo[*a*]carbazole (**12**)[15] were obtained. Use of decalin at 210 °C gave **10** and the fully aromatized product, 5-methoxy-11*H*-benzo[*a*]-carbazole (**13**), without removal of the methoxy group. See Scheme II.

Table I. Formation of Carbazoles by Thermal Reaction of 2,3-Divinylindoles

2,3-divinylindole	solvent	temp, °C	product	% yield
9	xylene	150	10	22
			11	16.9
	1,2-dichlorobenzene	180	10	22.9
			12	16.1
	decalin	210	10	20.2
			13	28.9
17	xylene	150	3	21
	1,2-dichlorobenzene	180	3	22
	decalin	210	3	48.5
25	decalin	210	4	47.4

This carbazole synthesis provides an efficient synthesis of hyellazole and 6-chlorohyellazole. Hydrolysis of the alcohol **14**, prepared by condensation of **5** with propiophenone as in the formation of **6**, afforded 2-(1-phenyl-1-propenyl)indole (**15**) as a single product (see Scheme III). Vilsmeier reaction of **15** followed by Wittig reaction of the indole 3-aldehyde **16** with (methoxymethylene)triphenylphosphorane yielded the 2,3-divinylindole **17**. This was heated in xylene in the presence of 5% Pd–C at 150 °C for 48 h to give hyellazole **3** in 21% yield.[1] The yield of **3** increased to 48.5% by heating **17** in decalin at 210 °C instead of xylene. The yields of products varied with temperature as summarized in Table I.

Furthermore, hydrolysis of the alcohol **19**, prepared by condensation of *N*-(benzenesulfonyl)-5-chloroindole (**18**) with propiophenone, afforded 5-chloro-2-(1-phenyl-1-propenyl)indole (**20**). Since the direct formylation of **20** by Vilsmeier reaction was not successful, the indole 3-aldehyde **24** was prepared as follows. Treatment of **20** with

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(12) J. H. Cardellina, II, M. O. Kirkup, R. E. Moore, J. S. Mynderse, K. Seff, and C. J. Simmons, *Tetrahedron Lett.*, **1979**, 4915.
(13) R. J. Sundberg and H. F. Russel, *J. Org. Chem.*, **38**, 3324 (1973). The procedure was slightly modified by using LDA instead of *t*-BuLi.
(14) (a) S. G. Levine, *J. Am. Chem. Soc.*, **80**, 6150 (1958); (b) S. Danishefsky, K. Nagasawa, and W. Wang, *J. Org. Chem.*, **40**, 1989 (1975).
(15) H. M. Grotta, C. J. Riggle, and A. E. Bearse, *J. Org. Chem.*, **26**, 1509 (1961).

oxalyl chloride followed by the reaction of the acid chloride **21** with ethanol gave the keto ester **22**. Decarboxylation[16] of the keto acid **23**, obtained from **22**, was carried out by heating with aniline in anisole to afford the indole 3-aldehyde **24**. Methoxymethylenylation of **24** with (methoxymethylene)triphenylphosphorane gave the 2,3-divinylindole **25**, which was heated in decalin in the presence of 5% Pd–C to yield 6-chlorohyellazole **4**. The spectral data of **4** were identical with those in the literature.[12]

Thus, thermal cyclization of 2,3-divinylindoles in the presence of 5% Pd–C was found to be a preparatively useful method for the synthesis of polysubstituted carbazoles.

Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Tetrahydrofuran (THF) was dried and distilled from $LiAlH_4$ before use. ^1H NMR spectra were recorded on a Varian T-60 instrument and ^{13}C NMR spectra were taken with a JEOL FX-100 spectrometer. Mass spectra were determined on a Hitachi RMU-7L instrument.

***N*-(Benzenesulfonyl)-2-(1-hydroxycyclohexyl)indole (6).** To a stirred solution of LDA (prepared from 28.6 mL of 1.5 M hexane solution of *n*-BuLi and 6 mL of diisopropylamine in 30 mL of THF) was added a solution of **5** (10 g, 38.9 mmol) in THF (50 mL) at 0 °C. After 30 min, to this solution was added a solution of cyclohexanone (4.2 g, 42.9 mmol) in THF (30 mL) at −78 °C. The reaction mixture was gradually warmed to room temperature and kept under stirring for 4 h. The mixture was poured into aqueous NH_4Cl solution and extracted with benzene. The extract was washed with water, dried over Na_2SO_4, and evaporated. Recrystallization of the resulting solid from ether gave **6** (10.5 g, 75.9%): mp 168–170 °C; mass spectrum, *m/e* 355 (M^+). Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96; N, 3.94. Found: C, 67.47; H, 5.91; N, 3.76.

2-(1-Cyclohexenyl)indole (7). A mixture of **6** (10 g, 28.2 mmol), 10% NaOH (10 mL), and EtOH (100 mL) was heated under reflux for 14 h. The solvent was evaporated and the remaining residue was extracted with benzene. The extract was washed with water, dried over Na_2SO_4, and evaporated. The resulting residue was chromatographed on silica gel. Elution with 2% ethyl acetate–hexane afforded **7** (2.7 g, 48.7%): mp 140–141 °C (benzene–hexane); mass spectrum, *m/e* 197 (M^+). Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.44; H, 7.64; N, 6.92.

2-(1-Cyclohexenyl)-3-formylindole (8). A mixture of DMF (3.5 mL) and $POCl_3$ (1.9 mL) was stirred at 25 °C for 30 min. To this solution was added a solution of **7** (2 g, 10.2 mmol) in DMF (10 mL). The mixture was stirred at 45 °C for 45 min and then poured into ice. The mixture was made basic with 10% NaOH to give yellowish precipitate, which was collected by filtration. Recrystallization from EtOH gave **8** (1.9 g, 83.3%): mp 228–230 °C; mass spectrum, *m/e* 225 (M^+); ^1H NMR ($CDCl_3$) δ 10.1 (1 H, s). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.80; H, 6.74; N, 5.94.

2-(1-Cyclohexenyl)-3-(β-methoxyvinyl)indole (9). To a suspension of (methoxymethyl)triphenylphosphonium chloride (0.7 g, 2.1 mmol) in THF (5 mL) was added *n*-BuLi (1.5 mL of a 1.5 M hexane solution) under ice-cooling. After the stirring had been continued for 30 min at the same temperature, to this solution was added a solution of **8** (0.2 g, 0.78 mmol) in THF (5 mL). After the stirring had been continued at room temperature for 14 h, the mixture was poured into water and extracted with benzene. The extract was washed with water, dried over Na_2SO_4, and evaporated. The resulting residue was used for the following reaction without purification because of unstability.

Dehydrogenative Thermal Cyclization of 9. Method A. A mixture of **9** (obtained from 0.2 g of **8**), 5% Pd–C (0.2 g), and xylene (30 mL) was refluxed at 150 °C for 48 h. The mixture was diluted with benzene, and 5% Pd–C was removed by filtration. The filtrate was evaporated and the resulting residue was separated by preparative TLC by using silica gel 60 PF_{254} and 10% ethyl acetate–hexane as an eluant. The upper layer afforded 1,2,3,4-tetrahydro-5-methoxy-11*H*-benzo[*a*]carbazole (**10**; 48.9 mg, 22%): mp 143–145 °C mass spectrum, *m/e* 251 (M^+), 251.1315 (calcd for $C_{17}H_{17}NO$, found 251.1312); ^1H NMR ($CDCl_3$) δ 1.87 (4 H, m), 2.80 (4 H, m), 3.90 (3 H, s). The lower layer gave 1,2,3,4-tetrahydro-11*H*-benzo[*a*]carbazole (**11**; 37.7 mg, 16.9%): mp 115–117 °C; mass spectrum, *m/e* 221 (M^+), 221.1203 (calcd for $C_{16}H_{15}N$, found 221.1199); ^1H NMR ($CDCl_3$) δ 1.93 (4 H, m), 2.90 (4 H, m).

Method B. A mixture of **9** (obtained from 0.2 g of **8**), 5% Pd–C (0.2 g), and 1,2-dichlorobenzene (30 mL) was heated at 180 °C for 48 h and worked up as above to yield **10** (51 mg, 22.9%) and 11*H*-benzo[*a*]carbazole (**12**) (31 mg, 16.1%): mp 225–227 °C (lit.[15] mp 228 °C).

Method C. A mixture of **9** (obtained from 0.2 g of **8**), 5% Pd–C (0.2 g), and decalin (30 mL) was heated at 210 °C for 48 h and worked up as above to give **10** (45 mg, 20.2%) and 5-methoxy-11*H*-benzo[*a*]carbazole (**13**; 63.4 mg, 28.9%): mp 133–137 °C; mass spectrum, *m/e* 247 (M^+), 247.0996 (calcd for $C_{17}H_{13}NO$, found: 247.0004); ^1H NMR ($CDCl_3$) δ 4.02 (3 H, s).

Alcohol 14. To a stirred solution of LDA (prepared from 14.1 mL of a 1.5 M hexane solution of *n*-BuLi and 3 mL of diisopropylamine in 20 mL of THF) was added a solution of **5** (5 g, 19.4 mmol) as above. After 30 min, to this solution was added a solution of propiophenone (2.88 g, 21.5 mmol) in 20 mL of THF at −78 °C. The mixture was gradually warmed to room temperature and kept for 4 h under stirring. The mixture was poured into aqueous NH_4Cl solution and extracted with ethyl acetate. The solvent was evaporated and the resulting residue was recrystallized from ether to give **14** (6 g, 86.3%): mp 168–170 °C; mass spectrum, *m/e* 391 (M^+). Anal. Calcd for $C_{23}H_{21}NO_3S$: C, 70.56; H, 5.41; N, 3.58. Found: C, 70.42; H, 5.40; N, 5.48.

2-(1-Phenyl-1-propenyl)indole (15). A mixture of **14** (5.5 g, 14.1 mmol), 10% NaOH (50 mL), EtOH (100 mL), and dioxane (50 mL) was heated under reflux for 14 h. The solvent was evaporated and the resulting residue was extracted with benzene. The extract was washed with water, dried over Na_2SO_4, and evaporated. The remaining residue was chromatographed on silica gel. Elution with 2% ethyl acetate–hexane yielded **15** (3.2 g, 88.2%): mp 87–89 °C (hexane); mass spectrum, *m/e* 233 (M^+); ^1H NMR ($CDCl_3$) δ 1.94 (3 H, d, J = 7 Hz). Anal. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00. Found: C, 87.73; H, 6.23; N, 5.91.

3-Formyl-2-(1-phenyl-1-propenyl)indole (16). To a solution of Vilsmeier reagent (prepared from 6 mL of DMF and 3.5 mL of $POCl_3$) was added a solution of **15** (3 g, 12.88 mmol) in DMF (10 mL), and the reaction mixture was stirred at 45 °C for 45 min. The mixture was poured into ice–water and made basic with 10% NaOH. The precipitate was collected and recrystallized from benzene to give **16** (2.86 g, 85%): mp 182–183 °C; mass spectrum, *m/e* 261 (M^+); ^1H NMR ($CDCl_3$) δ 9.74 (1 H, s). Anal. Calcd for $C_{18}H_{15}NO$: C, 82.75; H, 5.79; N, 5.36. Found: C, 82.56; H, 5.66; N, 5.24.

3-(β-Methoxyvinyl)-2-(1-phenyl-1-propenyl)indole (17). To a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (1.64 g, 4.81 mmol) in THF (5 mL) was added a solution of *n*-BuLi (3.1 mL of a 1.52 M hexane solution) at 0 °C. After the mixture was stirred at the same temperature for 30 min, a solution of **16** (0.5 g, 1.92 mmol) in THF (10 mL) was added, and after the stirring had been continued for 14 h, the mixture was poured into water and extracted with benzene. During the reaction, the flask was wrapped with foil to keep out light, since the product is light sensitive. The extract was washed with water, dried over Na_2SO_4, and evaporated. The remaining residue was used for the following reaction without purification because of unstability.

Hyellazole 3. Method A. A mixture of **17** (prepared from 0.5 g of **16** as above), 5% Pd–C (0.5 g), and xylene (30 mL) was refluxed at 150 °C for 48 h. The mixture was diluted with benzene and 5% Pd–C was filtered off. The filtrate was evaporated and the resulting residue was chromatographed on silica gel. Elution with 1% ethyl acetate–hexane gave **3** (115.4 mg, 21.0%): mp 133–134 °C (lit.[12] mp 133–134 °C); mass spectrum, *m/e* 287 (M^+); ^1H NMR (acetone-d_6) δ 2.15 (3 H, s), 3.95 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 152.7 (s), 139.5 (s), 133.3 (s), 129.1 (d), 128.4 (d), 125.5

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(s), 125.0 (d), 123.8 (s), 123.7 (s), 120.3 (s), 119.9 (d), 118.9 (d), 110.6 (d), 100.3 (d), and 56.2 (q); these data are identical with those in the literature.[12]

Method B. A mixture of **17** (obtained from 0.5 g of **16**), Pd–C (0.5 g), and 1,2-dichlorobenzene (30 mL) was heated at 180 °C for 48 h and worked up as above to give **3** (116 mg, 22%).

Method C. A mixture of **17** (obtained from 0.5 g of **16**), Pd–C (0.5 g), and decaline (30 mL) was heated at 210 °C for 48 h and worked up as above to yield **3** (244 mg, 48.5%).

***N*-(Benzenesulfonyl)-5-chloroindole (18).** To a suspension of NaH (60% suspension in oil; washed with petroleum ether before use) in THF (20 mL) was added a solution of 5-chloroindole (5 g, 33.1 mmol) in THF (50 mL). The solution was stirred until evolution of H_2 ceased (about 1 h) and then to this solution was added a solution of benzenesulfonyl chloride (6.4 g, 36.4 mmol) in THF (50 mL) under ice-cooling. After the stirring had been continued for 2 h at room temperature, the mixture was poured into water and extracted with ethyl acetate. The solvent was washed with water, dried over Na_2SO_4, and evaporated. The remaining residue was distilled to give **18** (8.5 g, 88.5%): bp 230–231 °C (1 torr); mp 47–48 °C; mass spectrum, m/e 291 (M^+). Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 57.63; H, 3.46; N, 4.80. Found: C, 57.64; H, 3.46; N, 4.78.

5-Chloro-2-(1-phenyl-1-propenyl)indole (20). To a stirred solution of LDA (prepared from 5 mL of a 1.53 M hexane solution of *n*-BuLi and 1.1 mL of diisopropylamine in 5 mL of THF) was added a solution of **18** (2 g, 6.87 mmol) in THF (20 mL) under ice-cooling. After the stirring had been continued for 30 min, a solution of propiophenone (1 g, 7.46 mmol) in THF (10 mL) was added to this solution at −78 °C. The mixture was gradually warmed to room temperature and kept for 4 h and then poured into aqueous NH_4Cl solution and extracted with ethyl acetate. The extract was washed with water, dried over Na_2SO_4, and evaporated. A mixture of the resulting residue, 10% NaOH (20 mL), EtOH (30 mL), and dioxane (30 mL) was refluxed for 14 h under stirring. The solvent was removed and extracted with benzene. The extract was washed with water and dried over Na_2SO_4. Removal of the solvent gave **20** (1.2 g, 65.4%) as a viscous oil; mass spectrum, m/e 267 (M^+), 269 ($M^+ + 2$), 267.0813 (calcd for $C_{17}H_{14}ClN$, found, 267.0801); ^1H NMR ($CDCl_3$) δ 1.60 (3 H, d, J = 7 Hz).

Keto Ester 22. To a solution of **20** (1 g, 3.75 mmol) in dry ether (20 mL) was added a solution of oxalyl chloride (0.5 g, 3.94 mmol) in dry ether (20 mL) at 0 °C under stirring. After the stirring had been continued for 2 h at room temperature, the solvent was evaporated and the resulting residue was dissolved in EtOH under ice-cooling and the solution was stirred at room temperature for 1 h. The solvent was evaporated and the remaining residue was chromatographed on silica gel. Elution with benzene afforded **22** (0.95 g, 69.1%): mp 152–153.5 °C (benzene–hexane); mass spectrum, m/e (M^+), 369 ($M^+ + 2$); ^1H NMR ($CDCl_3$) 1.17 (3 H, t, J = 7 Hz), 1.87 (3 H, d, J = 7 Hz), 4.03 (2 H, q, J = 7 Hz). Anal. Calcd for $C_{21}H_{18}ClNO_3$: C, 68.30; H, 4.93; N, 3.81. Found: C, 68.31; H, 4.79; N, 3.65.

5-Chloro-3-formyl-2-(1-phenyl-1-propenyl)indole (24). A mixture of **22** (0.8 g, 2.18 mmol), 10% NaOH (10 mL), and EtOH (20 mL) was refluxed for 1 h. The solvent was evaporated and the remaining residue was washed with ether and made acidic with dilute HCl. The mixture was extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and evaporated. A mixture of the resulting keto acid **23** and aniline (0.37 g) in anisole (20 mL) was heated at 140–145 °C under stirring until evolution of CO_2 ceased (about 1 h). Anisole was removed by distillation in vacuo and the remaining residue was acidified with dilute HCl and extracted with $CHCl_3$. The extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent left **24** (0.25 g, 38.9%): mp 207–209 °C (benzene); mass spectrum, m/e 295 (M^+), 297 ($M^+ + 2$); ^1H NMR ($CDCl_3$) δ 1.87 (3 H, d, J = 7 Hz), 9.82 (1 H, s). Anal. Calcd for $C_{18}H_{14}ClNO$: C, 73.09; H, 4.77; N, 4.74. Found: C, 73.22; H, 4.82; N, 4.68.

5-Chloro-3-(β-methoxyvinyl)-2-(1-phenyl-1-propenyl)-indole (25). To a solution of (methoxymethylene)triphenylphosphorane (prepared from 0.58 g of (methoxymethyl)triphenylphosphonium chloride and 1.35 mL of 1.25 M hexane solution of *n*-BuLi in 3 mL of THF) was added a solution of **24** (0.2 g, 0.68 mmol) in THF (5 mL) at 0 °C. After the stirring had been continued for 14 h at room temperature, the mixture was poured into water and extracted with benzene. The extract was washed with water, dried over Na_2SO_4, and evaporated. The remaining residue was used for the following reaction without purification because of unstability.

6-Chlorohyellazole (4). A mixture of **25** (prepared from 0.2 g of **24**), 5% Pd–C (0.2 g), and decalin (10 mL) was heated at 210 °C for 48 h. Decalin was distilled in vacuo and the residue was dissolved in benzene. After removal of 5% Pd–C by filtration, the solvent was evaporated. The resulting residue was purified by preparative TLC by using silica gel 60 PF_{254} and 10% ethyl acetate–hexane as an eluant to yield **4** (103 mg, 47.4% from **24**); mp 163–164 °C (lit.[11] mp 163–164 °C); mass spectrum, m/e 321 (M^+), 323 ($M^+ + 2$); ^1H NMR (acetone-d_6) δ 2.15 (3 H, s), 3.96 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 153.0 (d), 137.7 (s), 133.9 (d), 129.8 (d), 129.1 (d), 127.8 (d), 125.8 (s), 125.3 (s), 124.9 (d), 124.3 (s), 119.1 (s), 119.6 (d), 111.6 (d), 100.1 (d), 56.1 (q), 13.1 (q); these spectral data were identical with those in the literature.[12]

Registry No. **3**, 74364-11-7; **4**, 74364-10-6; **5**, 40899-71-6; **6**, 78329-39-2; **7**, 78329-40-5; **8**, 78329-41-6; **9**, 78329-42-7; **10**, 78329-43-8; **11**, 78329-44-9; **12**, 239-01-0; **13**, 78329-45-0; **14**, 77092-50-3; **15**, 78329-46-1; **16**, 77092-51-4; **17**, 77092-52-5; **18**, 78329-47-2; **19**, 78329-48-3; **20**, 78329-49-4; **21**, 78329-50-7; **22**, 78329-51-8; **23**, 78329-52-9; **24**, 78329-53-0; **25**, 78329-54-1; cyclohexanone, 108-94-1; (methoxymethyl)triphenylphosphonium chloride, 4009-98-7; propiophenone, 93-55-0; 5-chloroindole, 17422-32-1; benzenesulfonyl chloride, 98-09-9; oxalyl chloride, 79-37-8.