

(1 g) was dissolved in hot methylene chloride-petroleum ether (bp 60–70°). Upon cooling the solution and careful evaporation of solvent, four fractions of crystals were obtained, mp 192–193, 195–204, 195–206, 204–206°, respectively. The Mössbauer spectrum of each sample was a singlet resonance at 1.23 ± 0.06 mm/sec. The highest melting fraction was a pale yellow-green solid. This experiment was repeated with an authentic sample of III, prepared as in ref 2 with identical results.

Anal. Calcd for $C_{30}H_{26}Sn$: C, 71.35; H, 5.19; Sn, 23.50; mol wt, 505. Found: C, 71.86; H, 5.21; Sn, 23.12, Cl, 0.00; mol wt, 516.

A similar reaction produced a white solid (mp, 196–197°) in 70% yield whose nmr spectrum contained a singlet resonance at τ 9.44 and the phenyl multiplet centered at 3.0. The ^{119m}Sn Mössbauer spectrum was a doublet. The (1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin chloride¹⁰ structure is consistent with these data.

Anal. Calcd for $C_{30}H_{27}SnCl$: C, 66.51; H, 5.02; Cl, 6.55; Sn, 21.9; mol wt, 541.2. Found: C, 65.94; H, 4.92; Cl, 5.13; Sn, 21.95; mol wt, 521.

Octaphenyl-1,1'-spirobistannole (II) from 1,1-Dimethyl-2,3,4,5-tetraphenylstannole (III).—Compound III (0.008 mol) in 60 ml of anhydrous THF was slowly added to 60 ml of a suspension of I (0.023 mol) and stirred for 3 hr under nitrogen. After addition of water the organic layer gave a yellow solid (1 g, 25% yield based on I) identical with II. None of the stannole compound could be isolated from the remaining oil.

Cleavage Reaction of Diethyltin Dichloride.—Diethyltin dichloride (0.032 mol) in 150 ml of THF was added to I (0.075 mol) in 200 ml ether. Near the end of the addition the solution turned from a dark green to a deep yellow-brown. After 1 hr of stirring, carbon dioxide was passed through the solution, producing a short-lived, deep red color. Water was added and the organic layer was separated and dried over calcium sulfate. The solvent was removed to give II after recrystallization from methylene chloride-petroleum ether (4 g, 13% yield based on I). The remaining oil resisted further recrystallization.

1,1-Divinyl-2,3,4,5-tetraphenylstannole.—To I (0.075 mol) in 200 ml of ether was slowly added divinyltin dichloride (0.041 mol) in 100 ml of ether. After 1 hr of stirring, the solvent was removed and 15 g of yellow solid (42% yield based on I) was isolated. The residue was recrystallized from methylene chloride and washed with several portions of 1:1 benzene-petroleum ether to give pale yellow crystals, mp 154–156°. None of the more insoluble spiro compound was found. The mass spectrum contained a series of peaks corresponding in distribution of intensities to the relative abundances of the tin isotopes with the m/e value of the ^{120}Sn peak = 530; calcd for $C_{32}H_{28}Sn$: 530. The ir spectrum contained prominent bands at 3000, 1580, 1475, 1000, 950, 790, 780, 760, 700, and 478 cm^{-1} . Subsequent reactions run in THF gave a yellow solid, mp 265–270°, with ir and nmr spectra identical with that of an authentic sample of II.

Anal. Calcd for $C_{32}H_{28}Sn$: C, 72.59; H, 4.91; Sn, 22.49; mol wt, 529. Found: C, 73.29; H, 5.10; Sn, 21.57; Cl, 0.00; mol wt, 570.

Cleavage Reaction of Trimethyltin Chloride.—Compound I (0.075 mol) was prepared as described above, excess lithium chips were removed, and 450 ml of THF was added. Trimethyltin chloride (0.057 mol) was added in 200 ml of ether. A yellow solid formed near the end of the addition whose ir and nmr spectra were identical with those of II (25 g, 80% yield based on I, mp 268–270°). Solvents were vacuum evaporated and some tetramethyltin was isolated by fractional distillation.

Cleavage Reaction of Tri-*n*-butyltin Chloride.—Compound I (0.075 mol) was prepared as described above, excess lithium chips were removed, and 450 ml of THF was added. Tri-*n*-butyltin chloride (0.074 mol) dissolved in 200 ml of ether was added dropwise, but the green color of the dilithium reagent remained until additional tri-*n*-butyltin chloride (0.077 mol) was added, at which time a yellow color appeared. Water (50 ml) was added and the organic layer separated to yield II (mp 265–270°, 8 g, 27% yield based on I).

Hexaphenylplumbole.—An ethereal suspension of diphenyllead dichloride (300 ml, 0.02 mol) was mixed with I (200 ml, 0.05 mol) in ether and stirring was continued for 4 days. Water (100 ml) was added, and yellow crystals (1.83 g, 15% yield based on diphenyllead dichloride), mp 153–155°, were obtained after evaporation of the ether layer and recrystallization from methylene chloride. Sublimation *in vacuo* and column chromatography on silica gel resulted in decomposition. The ir spectrum con-

tained prominent bands at 3090, 1610, 1575, 1490, 1443, 1075, 1020, 1000, 781, 763, 738, and 687 cm^{-1} and was very similar to that of the tin analog.

Anal. Calcd for $C_{40}H_{30}Pb$: C, 66.95; H, 4.18; mol wt, 717. Found: C, 66.6; H, 4.16; mol wt, 770.

1,1-Dimethyl-2,3,4,5-tetraphenylgermole.—This white crystalline compound, mp 183–184°, prepared by the method of Gilman, *et al.*,³ was recrystallized from petroleum ether (bp 60–70°) and sublimed *in vacuo* at 175°. The nmr spectrum contained a resonance at τ 9.37 in addition to that owing to the phenyl protons, and the ir spectrum showed prominent bands at 3100, 3040, 1605, 1490, 1445, 1080, 1035, 834, 819, 789, 709, and 697 cm^{-1} . High resolution mass spectral data gave for the monogermanium molecular ion at mass 458 an exact mass of 460.1239 based on ^{72}Ge (calcd for $C_{30}H_{26}^{72}Ge$: 460.1244).

Anal. Calcd for $C_{30}H_{26}Ge$: C, 78.50; H, 5.66; Ge, 15.83. Found: C, 78.32; H, 5.80; Ge, 15.91.

Registry No.—I, 21289-08-7; II, 21779-48-6; III, 20195-60-2; dimethyltin dichloride, 753-73-1; diethyltin dichloride, 866-55-7; divinyltin dichloride, 7532-85-6; 1,1-divinyl-2,3,4,5-tetraphenylstannole, 21779-52-2; trimethyltin chloride, 1066-45-1; tri-*n*-butyltin chloride, 1461-22-9; hexaphenylplumbole, 21779-54-4; 1,1-dimethyl-2,3,4,5-tetraphenylgermole, 20991-88-2; (1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin chloride, 21779-56-6; 9,9-diphenyl-9-stannafluorene, 5381-63-5; hexaphenylstannole, 21813-34-3.

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A Synthesis of Norisotuboflavine

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The β -carboline alkaloids flavocarpine (1),¹ tuboflavine (2),² isotuboflavine (3),³ norisotuboflavine (4),³ and methyl β -carboline-1-carboxylate (5)³ are minor constituents of *Pleiocarpa tubicina* Benth. Syntheses of flavocarpine,¹ tuboflavine,⁴ and methyl β -carboline-1-carboxylate⁵ have been reported. In this note we describe a synthesis of norisotuboflavine (4) from the companion alkaloid 5. Very recently Rosenkranz and Schmid reported a synthesis of 4 from 4,5-dihydrocanthin-6-one,⁶ which is available synthetically in low yield from DL-tryptophan.^{4,6} Inasmuch as carboline

(1) G. Büchi, R. E. Manning, and F. A. Hochstein, *J. Amer. Chem. Soc.*, **84**, 3393 (1962).

(2) C. Kump, J. Seibl, and H. Schmid, *Helv. Chim. Acta*, **46**, 498 (1963).

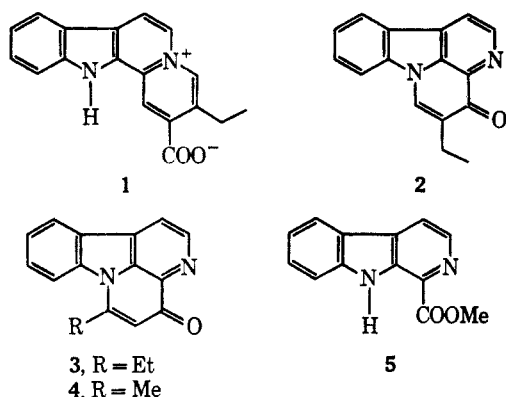
(3) H. Achenbach and K. Biemann, *J. Amer. Chem. Soc.*, **87**, 4177 (1965).

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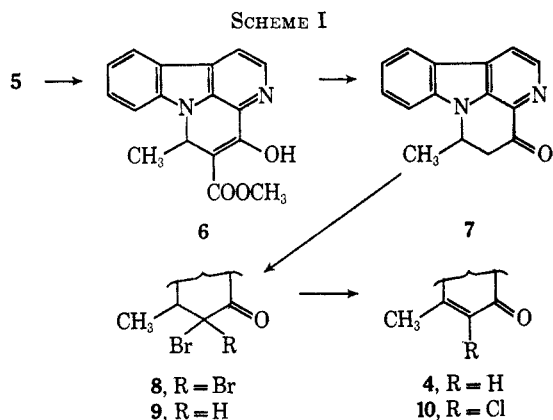
(5) H. R. Synder, H. G. Walker, and F. X. Werber, *J. Amer. Chem. Soc.*, **71**, 527 (1949).

(6) H. J. Rosenkranz and H. Schmid, *Helv. Chim. Acta*, **51**, 565 (1968).

ester **5** is also prepared from DL-tryptophan,⁵ the two syntheses of **4** proceed from a common starting material, but differ in their approach to the elaboration of the ketonic ring.



Our synthesis of **4** was predicated on the concept that Michael addition of the conjugate base of **5** onto an acrylic derivative would generate the anion required for the Dieckmann condensation, which in turn would furnish the indolo[3,2,1-*de*][1,5]naphthyridine ring system characteristic of **2-4**. The potential of this procedure for the present purpose was suggested by its utility for the fabrication of the pyrrolo[1,2-*a*]indole ring system.⁷ As expected, treatment of **5** with sodium hydride and methyl crotonate in tetrahydrofuran gave 29% of the highly fluorescent β -keto ester **6** (see Scheme I); spectral data indicate that this substance exists in the enolic form in solution. Acid-catalyzed decarboxylation of **6** afforded 82% of dihydronorisotuboflavine (**7**).



Introduction of the unsaturation required for the conversion of **7** into norisotuboflavine (**4**) was accomplished only after considerable difficulty. Initial efforts to effect this transformation with selenium dioxide, a reagent used with success by Schmid and his collaborators⁴ for the preparation of **2** from 5-ethyl-4,5-dihydrocathine, proved unrewarding. Equally unsuccessful were the dehydrogenation agents chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and manganese dioxide.

Accordingly, conversion of **7** into α -bromoketone **9**, from which **4** could be secured by dehydrohalogenation, was investigated intensively. Direct bromination of **7** failed, apparently as a result of perbromide formation. Attempts to activate the α position of **7** toward halogenation through formation of an enamine and an enol acetate under neutral or acidic conditions were unsuccessful. Moreover, base-catalyzed acylation of **7** with ethyl formate and ethyl oxalate failed to give a hydroxymethylene and an ethoxalyl derivative, respectively. Finally, direct formation of a hydroxymethylene derivative by condensation of the conjugate base of **5** with crotonaldehyde also failed. However, halogenation of **7** with trimethylphenylammonium perbromide⁸ ultimately served to affect the desired transformation, albeit in low yield.

Initially, treatment of **7** with a molar equivalent of this reagent afforded the *gem*-dibromide **8**, in addition to 41% of the hydrobromide of **7**. Treatment of **8** with lithium chloride in dimethylformamide afforded 31% (from **7**) of the α -chloro- α,β -unsaturated ketone **10**. The formation of **8** under the above halogenation conditions appears to be the result of combination of unreacted **7** with hydrogen bromide liberated in the bromination process; precipitation of the hydrobromide of **7** then results in an excess of halogenation reagent for the available ketone. This result suggested the use of potassium chlorate in combination with trimethylphenylammonium perbromide,⁹ in these circumstances the liberated bromide ion would be converted into bromine, and precipitation of the hydrobromide of **7** would be circumvented. Indeed, treatment of **7** with increments of trimethylphenylammonium perbromide and potassium chlorate resulted in the disappearance of ketone **7** (tlc) without formation of its hydrobromide. Dehydrobromination of the crude α -bromoketone **9** with lithium chloride in dimethylformamide then furnished norisotuboflavine (**4**) in low overall yield (4%). The alkaloid prepared in this manner gave satisfactory elemental analyses, and the ultraviolet, infrared, and nmr spectral properties were in excellent accord with those reported for the natural material. However, the mass spectrum of our synthetic material indicated the presence of trace amounts of monochloro and monobromo derivatives of **4**. These components are the apparent result of limited formation of *gem*-dibromide **8** under the conditions used for halogenation of **7**.

Experimental Section

General.—Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. The infrared (ir) spectra were determined in pressed potassium bromide disks with a Perkin-Elmer spectrophotometer, and the ultraviolet (uv) spectra were determined in methanol solution using a Cary recording spectrophotometer. Nmr spectra were determined in the indicated solvent on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The mass spectrum was determined with an A.E.I. MS-9 spectrometer. All evaporations were carried out under reduced pressure.

β -Carboline-1-carboxylic Acid.—The following procedure for the preparation of this acid from benzalharman represents an improvement over the procedure previously used for this conversion.⁵

(8) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

(9) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 927.

(7) G. R. Allen, Jr., J. F. Poletto, and M. J. Weiss, *J. Amer. Chem. Soc.*, **86**, 3877 (1964); *J. Org. Chem.*, **30**, 2897 (1965).

To a stirred solution of 4.03 g (0.015 mol) of benzalharman⁶ in 100 ml of acetone at -13° was added portionwise 4.98 g (0.0315 mol) of potassium permanganate over a period of 90 min. The mixture was stirred an additional 45 min at -12° , treated with 10 ml of ethanol, and evaporated to dryness. The residue was suspended in 200 ml of water and this mixture was acidified with concentrated hydrochloric acid in an ice bath. Sodium bisulfite was added portionwise to the stirred mixture until the dark solid dissolved. The resulting yellow solid was collected by filtration and washed with water to give 2.78 g (87%) of β -carboline-1-carboxylic acid, mp 245–247 $^{\circ}$ dec (lit.⁵ mp 235 $^{\circ}$).

Methyl 4-Hydroxy-6-methyl-6H-indolo[3,2,1-de][1,5]naphthyridine-5-carboxylate (6).—To a stirred, ice-cooled solution of 4.00 g (17.7 mmol) of methyl β -carboline-1-carboxylate⁶ in 250 ml of tetrahydrofuran was added 1.06 g (26.6 mmol) of a sodium hydride in mineral oil dispersion (60.2% concentration). The temperature was allowed to rise to ambient temperature with stirring during 3 hr, and the mixture was treated with 2.66 g (26.6 mmol, 2.7 ml) of methyl crotonate. The resulting mixture was heated at reflux temperature for 66 hr and then an additional 2.7 ml of methyl crotonate was added. Reflux was continued, and additional 2.7-ml portions of methyl crotonate were added at the end of 74 and 92 hr. Heating was discontinued after 114 hr. The cooled mixture was treated with 4.5 ml of glacial acetic acid and evaporated. Toluene was added to the residue and removed by evaporation; this process was repeated several times. The residue was extracted several times with ether and with acetone. The combined extracts were evaporated, and the residue was chromatographed on diatomaceous silica using a heptane-methanol (1:1) system. The fraction with peak hold-back volume 4.0 ($V_m/V_s = 2.21$) was evaporated to give 2.30 g of yellow solid, which was recrystallized from dilute acetone to give 1.49 g (29%) of yellow crystals, mp 163–168 $^{\circ}$.

A similar preparation, recrystallized several times from acetone-water, melted at 171–173 $^{\circ}$ dec; uv max 245, 285, 322, 375, 383 $m\mu$ (ϵ 24,700, 12,100, 6300, 9100, 8200); ir 2970, 1655, 1635, 1610, 1265 cm^{-1} ; nmr ($CDCl_3$) δ 10.3 (broad, 1, OH), 8.17–7.09 (m, 6, aryl H), 5.68 (q, 1, $J = 6$ Hz, 6 H), 3.96 (s, 3, $COOCH_3$), 1.45 (d, 2, $J = 6$ Hz, 6 CH_3).

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.37; H, 4.80; N, 9.52. Found: C, 68.95; H, 4.96; N, 9.42.

5,6-Dihydro-6-methyl-4H-indolo[3,2,1-de][1,5]naphthyridin-4-one (7).—A solution of 1.51 g (5.15 mmol) of methyl 4-hydroxy-6-methyl-6H-indolo[3,2,1-de][1,5]naphthyridine-5-carboxylate (6) in 20 ml of acetic acid and 80 ml of 3 *N* hydrochloric acid was heated at reflux for 3 hr, cooled, and added to 65 ml of concentrated ammonium hydroxide mixed with ice. The mixture was extracted with methylene chloride and the extracts were washed with 10% sodium hydroxide solution and water. The dried ($MgSO_4$) extract was evaporated to give a yellow glass. This residue was crystallized from acetone-hexane to give in two crops 953 mg (82%) of yellow needles, mp 141–144 $^{\circ}$.

A similar preparation, recrystallized twice from acetone-hexane, melted at 143–144 $^{\circ}$; uv max 250, 268, 288, 312, 372 $m\mu$ (ϵ 13,200, 8950, 12,700, 8400, 5200); ir 1695, 1620 cm^{-1} ; nmr ($CDCl_3$) δ 8.64 (d, 1, $J = 5.0$ Hz, 1 H), 8.05 (d, 1, $J = 5.0$ Hz, 2 H), 8.34–7.25 (m, 4, aryl H), 5.13 (m, 1, $J_{H_6-H_{10a}} = 6.5$ Hz, $J_{H_6-H_{10e}} = 2.0$ Hz, $J_{H_6-CH_3} = 6.5$ Hz, 6 H), 3.50 (q, 1, $J_{H_{10a}-H_6} = 6.5$ Hz, $J_{gem} = 16.3$ Hz, 5 H), 3.08 (q, 1, $J_{H_{10e}-H_6} = 2.0$ Hz, $J_{gem} = 16.3$ Hz, 5e H), 1.42 (d, 3, $J_{CH_3-H_6} = 6.5$ Hz, 6 CH_3).

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.39; H, 5.36; N, 11.96.

5-Chloro-6-methyl-4H-indolo[3,2,1-de][1,5]naphthyridin-4-one (10).—A solution of 800 mg (3.4 mmol) of 5,6-dihydro-6-methyl-4H-indolo[3,2,1-de][1,5]naphthyridin-4-one (7) and 1.28 g (3.4 mmol) of trimethylphenylammonium perbromide in 24 ml of tetrahydrofuran was stirred for 4 hr, and the resulting mixture was filtered to give 1.05 g of orange crystals. This solid was dissolved in 40 ml of water, and the resulting solution was rendered alkaline with concentrated ammonium hydroxide and filtered to give 330 mg (41%) of 7 as yellow crystals, mp 139–141 $^{\circ}$.

The tetrahydrofuran filtrate was stirred for an additional 18 hr at room temperature; the mixture was filtered to give 575 mg of orange crystals, mp $>300^{\circ}$ (darkening from 180 $^{\circ}$). Material from a similar experiment had mp $>300^{\circ}$; ir 1645, 1600 cm^{-1} .

Anal. Calcd for $C_{18}H_{10}Br_2N_2O$: Br, 40.56. Found: Br, 40.78.

A solution of 810 mg (2.06 mmol) of dibromo ketone prepared in the above manner and 0.8 g of lithium chloride in 80 ml of dimethylformamide was stirred at 100 $^{\circ}$ for 18 hr. The solution was evaporated, and the evaporation was repeated several times with toluene. The residual solid was dissolved in water, rendered alkaline with concentrated ammonium hydroxide, and extracted with methylene chloride. The extracts were washed with water and evaporated. The residue was dissolved in ethanol and this solution was evaporated; this procedure was repeated several times. The residue was triturated with acetone to give 350 mg of yellow crystals, mp 270–275 $^{\circ}$.

This material was chromatographed on a column prepared from 100 g of a synthetic magnesia-silica gel adsorbent and methylene chloride. The acetone and methanol-acetone (1:4) eluates were evaporated to give 230 mg of yellow crystals. This material was recrystallized from acetone-ethanol to afford 171 mg (31% from unrecovered 7) of yellow needles, mp 283–284 $^{\circ}$ dec; uv max 215, 262, 288, 323, 390 $m\mu$ (ϵ 42,500, 29,000, 26,900, 7000, 11,300); ir 1650, 1625, 1615, 1545 cm^{-1} ; nmr (CF_3CO_2H) δ 9.22 (d, 1, $J = 6.0$ Hz, 1 H) 8.90 (d, 1, $J = 6.0$ Hz, 2 H), 8.51–7.67 (m, 4, aryl H), 3.42 (s, 3, 6 CH_3).

Anal. Calcd for $C_{16}H_9ClN_2O$: C, 67.02; H, 3.38; Cl, 13.19; N, 10.42. Found: C, 66.59; H, 3.41; Cl, 13.13; N, 10.09.

Norisotuboflavine (6-Methyl-4H-indolo[3,2,1-de][1,5]naphthyridin-4-one (4)).—To a solution of 625 mg (2.65 mmol) of 5,6-dihydro-6-methyl-4H-indolo[3,2,1-de][1,5]naphthyridin-4-one (7) in 13 ml of tetrahydrofuran was added a solution of 41 mg (0.34 mmol) of potassium chlorate in 6.5 ml of water. To the stirred, ice-cooled solution was added dropwise a solution of 543 mg (1.44 mmol) of trimethylphenylammonium perbromide in 13 ml of tetrahydrofuran. The solution was stirred at room temperature for 48 hr and then a solution of 132 mg (1.07 mmol) of potassium chlorate in 13 ml of water and a solution of 543 mg (1.44 mmol) of trimethylphenylammonium perbromide in 13 ml of tetrahydrofuran was added. The mixture was stirred an additional 18 hr, and then poured into 500 ml of water. The aqueous solution was extracted with methylene chloride. The extracts were washed with water, dried with magnesium sulfate, and evaporated to give 820 mg of crude bromo ketones as a gum.

A solution of this material in 50 ml of dry dimethylformamide was treated under argon with 950 mg of lithium chloride at 100 $^{\circ}$ for 90 min. The cooled solution was diluted with water and extracted with methylene chloride. The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to give 340 mg of residue. This material was chromatographed on 75 g of a synthetic magnesia-silica gel adsorbent. The methanol-acetone (3:7) eluate was evaporated to give 75 mg of yellow crystals exhibiting a single bright blue fluorescent spot on tlc in benzene-acetone-water (1:3:2). Sublimation of this material at 4–10 μ and 187 $^{\circ}$ gave 28.6 mg of yellow crystals. This solid was recrystallized from methanol to give 12.5 mg of yellow crystals, mp 294–296 $^{\circ}$ dec (lit.^{3,6} 282–284 $^{\circ}$, 298–300 $^{\circ}$); uv max 260, 282, 321, 385 $m\mu$ (ϵ 28,000, 26,200, 6100, 11,200); uv min 238, 269, 305, 345 $m\mu$ (ϵ 10,300, 18,000, 4900, 2300); uv inf 225 $m\mu$ (ϵ 19,200); ir 1640, 1610, 1565 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 234 (100), 206 (8), 205 (17), 168 (45), 166 (7), 139 (7), 103 (12), 67 (27). Minor molecular ions were also noted at 312 (monobromo species) and 258 (monochloro species).

Anal. Calcd for $C_{18}H_{10}N_2O$: C, 76.91; H, 4.30; N, 11.96. Found: C, 76.66; H, 4.36; N, 11.81.

Concentration of the filtrate gave an additional 11.8 mg (4%) of yellow crystals, mp 288–295 $^{\circ}$ dec, having spectral properties identical with those of the above material.

Anal. Found: C, 76.81; H, 4.32; N, 11.76.

Acknowledgment.—Microanalyses, spectral data, and partition chromatography were performed by Messrs. L. Brancone, W. Fulmor, C. Pidacks, and their associates, respectively. Generous supplies of methyl β -carboline-1-carboxylate were prepared by Messrs. A. Meyer and E. K. Norton with the cooperation of Dr. P. J. Kohlbrenner.

Registry No.—4, 21615-67-8; 6, 21615-68-9; 7, 21615-69-0; 8, 21615-70-3; 10, 21615-71-4.