25.14 (t); IR 1346, 1518, 1701 cm$^{-1}$; HRMS calcd for $C_{13}H_{15}NO_3$ 233.10520, obsd $m/z$ 233.10457; GCMS $m/z$ (relative intensity) 233 ($M^+$, 83), 136 (9), 97 (100).

**2-((4-Nitrophenyl)methyl)cyclopentanone (7a).** Compound **7a** was isolated as white crystals: mp 56 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.098 (d, $J$ = 8.7 Hz, 2 H), 7.299 (d, $J$ = 8.7 Hz, 2 H), 3.190 (dd, $J$ = 13.8, 4.5 Hz, 1 H), 2.640 (dd, $J$ = 13.8, 9.0 Hz, 1 H), 2.400–2.297 (m, 2 H), 2.138–1.909 (m, 3 H), 1.811–1.652 (m, 1 H), 1.490 (ddd, $J$ = 23.1, 10.8, 3.3 Hz, 1 H); $^{13}$C NMR $\delta$ ($CDCl_3$) 218.84 (s), 147.85 (s), 146.39 (s), 129.60 (d), 123.50 (d), 50.36 (d), 37.77 (t), 35.25 (t), 28.98 (t), 20.36 (t); IR 1342, 1518, 1731 cm$^{-1}$; HRMS calcd for $C_{12}H_{13}NO_3$ 219.08954, obsd $m/z$ 219.08927; GCMS $m/z$ (relative intensity) 219 ($M^+$, 79), 136 (15), 83 (56), 40 (100).

**2-((4-Nitrophenyl)methyl)cycloheptanone (7c).** Compound **7c** was isolated as white needles: mp 130 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.053 (d, $J$ = 8.4 Hz, 2 H), 7.252 (d, $J$ = 8.4 Hz, 2 H), 3.147–3.080 (dd, $J$ + 13.6, 6.6 Hz, 1 H), 2.85–2.95 (m, 1 H), 2.632–2.562 (dd, $J$ = 13.5, 7.4 Hz, 1 H), 2.399–2.366 (m, 2 H), 1.783–1.183 (m, 8 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 214.15 (s), 148.11 (s), 146.43 (s), 129.88 (d), 123.51 (d), 53.04 (d), 43.32 (t), 37.63 (t), 30.85 (t), 29.10 (t), 29.06 (t), 23.88 (t); IR 1348, 1520, 1699 cm$^{-1}$; HRMS calcd for $C_{14}H_{17}NO_3$ 247.12084, obsd $m/z$ 247.12082.

**3,4-Dihydro-2-((4-nitrophenyl)methyl)-1(2*H*)-naphthalenone (8).** To the enamine 4 (478 mg) and 170 $\mu$L of $Et_3N$ dissolved in 25 mL of DMF was added *p*-nitrobenzyl chloride (206 mg). The reaction mixture was irradiated for 80 min with a 275-W sunlamp before being poured into 200 mL of water containing 3.6 mmol of HCl. After being stirred for 12 h the mixture was extracted with three 30-mL volumes of $CH_2Cl_2$ and the extract dried over $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash column chromatography to yield after recrystallization from cyclohexane 141 mg of 8 (42%): mp 150 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.122 (d, $J$ = 8.7 Hz, 2 H), 8.016 (d, $J$ = 7.8 Hz, 1 H), 7.447 (t, $J$ = 7.5 Hz, 1 H), 7.380 (d, $J$ = 8.4 Hz, 2 H), 7.286 (t, $J$ = 7.5 Hz, 1 H), 7.201 (d, $J$ = 7.8 Hz, 1 H), 3.54–3.46 (m, 1 H), 2.97–2.93 (m, 2 H), 2.86–2.73 (m, 2 H), 2.12–2.01 (m, 1 H), 1.87–1.71 (m, 1 H); IR 1348, 1520, 1678 cm$^{-1}$. Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.24; H, 5.59; N, 4.99.

**2-(1-Methyl-1-nitroethyl)cyclohexanone (5).**[18] Compound **5** was obtained a solid: mp 52 °C; the $^1$H NMR agreed with the literature values; $^{13}$C NMR ($CDCl_3$) $\delta$ 208.07 (s), 88.55 (s), 57.19 (d), 42.68 (t), 29.67 (t), 27.58 (t), 25.26 (t), 24.89 (q), 22.61 (q); GCMS $m/z$ (relative intensity) 139 (59), 98 (0.6), 95 (72), 69 (100); Cl-MS ($NH_3$) 203 (M + $NH_4^+$, 100).

**4-((4-Nitrophenyl)methyl)morpholine (10b).**[19] Isolated material had the following properties: $^1$H NMR ($CDCl_3$) $\delta$ 8.154 (d, $J$ = 8.7 Hz, 2 H), 7.500 (d, $J$ = 8.7 Hz, 2 H), 3.698 (t, $J$ = 4.8 Hz, 4 H), 3.563 (s, 2 H), 2.433 (t, $J$ = 4.8 Hz, 4 H); IR ($CDCl_3$) 1346, 1522, 1115, 1265 cm$^{-1}$; GCMS $m/z$ (relative intensity) 222 ($M^+$, 85), 136 (100), 100 (27), 86 (60).

**1-((4-Nitrophenyl)methyl)pyrrolidine (9b).**[20] Isolated material had the expected $^1$H NMR: GCMS $m/z$ (relative intensity) 206 ($M^+$, 58), 205 (100), 136 (10), 84 (86).

**Other Reaction Products.** 1-Nitro-4-(1,1,2-trimethyl-2-nitropropyl)benzene[21] and diethyl ethyl(1-methyl-1-nitroethyl)-malonate[22] were prepared by literature procedures. Diethyl isopropylidenemalonate was isolated and compared with an authentic sample from Aldrich Chemical Co.: $^1$H NMR ($CDCl_3$) $\delta$ 4.21 (q, $J$ = 7.2 Hz, 4 H), 2.04 (s, 6 H), 1.26 (t, $J$ = 7.2 Hz, 6 H).

**Supplementary Material Available:** $^1$H NMR spectrum for **6** and $^{13}$C NMR spectra for **7a–c** (5 pages). Ordering information is given on any current masthead page.

(18) Russell, G. A.; Hershberger, J.; Owens, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312.
(19) Kirkpatrick, D. L.; Johnson, K. E.; Sarlorelli, A. C. *J. Med. Chem.* **1986**, *29*, 2048.
(20) Matter, O. Swiss Patent no. 268,094, Aug. 1, 1950.
(21) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725.
(22) Russell, G. A.; Norris, R. K.; Panek, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5839.

# A New Route to 9,9a-Dihydro-3*H*-pyrrolo[1,2-*a*]indoles via Radical Cyclization

Frederick E. Ziegler* and Lucio O. Jeroncic

*Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511-8118*

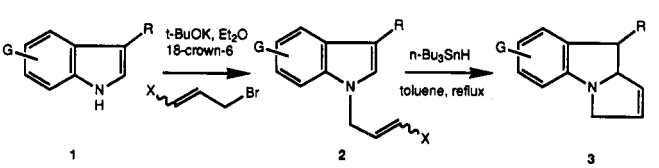
*Received November 30, 1990*

A new method for the preparation of 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indoles, an important substructure for the synthesis of mitomycins, is presented. A number of representative indoles are allylated on nitrogen with 1,3-dihalopropenes followed by *n*-$Bu_3SnH$-mediated radical cyclization. The effect of the substitution patterns of the indoles and reaction conditions is explored. In all reactions the products of cyclization predominate; however, uncyclized materials are produced along with isomers and oxidation products of the cyclized substances.

## Introduction

The development of methods for the synthesis of the 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indole **3** nucleus has been a challenge in the chemistry of the mitomycins.[1] Danishefsky[2] and Naruta[3] have reported methods that form both C–N bonds of the pyrrolo ring. The cyclization of terminal vinyl radicals with isolated olefins to form cyclopentenes has been reported by Beckwith,[4] Parsons,[5] and Hart.[6] Owing to the ready availability of the indole nucleus and the ease with which it can be N-allylated, we chose to explore the reaction sequence of Scheme I. During the course of these studies, Beckwith[7] reported the

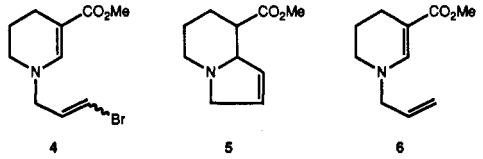
**Scheme I**




(1) For reviews on earlier synthetic efforts directed toward the mitosanes, see: (a) Kametani, T.; Takahashi, K. *Heterocycles* **1978**, *9*, 293. (b) Takahashi, K.; Kametani, T. *Heterocycles* **1979**, *13*, 411. (c) Franck, R. W. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 1.
(2) Danishefsky, S.; Berman, E. M.; Ciufolini, M.; Etheredge, S. J.; Segmuller, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 3891.
(3) Naruta, Y.; Nagai, N.; Maruyama, K. *J. Chem. Soc., Perkin Trans. I* **1988**, 1143.
(4) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525.
(5) Neary, A. P.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1090.
(6) Ghosh, T.; Hart, H. *J. Org. Chem.* **1989**, *54*, 5073.

0022-3263/91/1956-3479$02.50/0 

cyclization of the radical derived from vinyl bromide **4** afforded both the cyclization product **5** and the product of reduction **6**. We present here a convenient and relatively efficient method for the preparation of the dihydropyrroloindole nucleus based on the cyclization of terminal vinyl radicals with the heterocyclic ring of indoles.



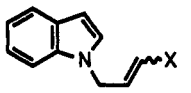
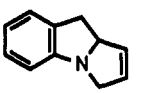
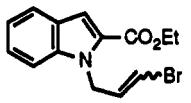
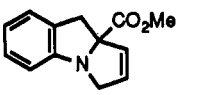
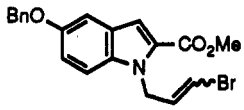
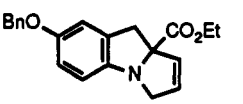
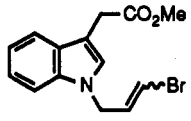
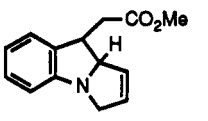
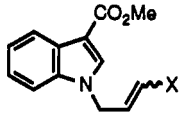
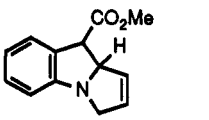
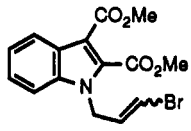
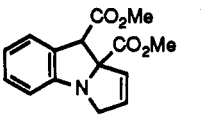
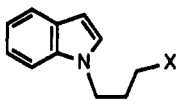
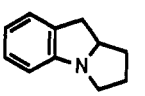
4 5 6

## Results and Discussion

The simple *N*-allylindole derivatives **7a** (Table I) served as the prototype for these reactions. The conditions of Guida and co-workers[8] were applicable for the N-alkylation procedure. Thus, the allylation of indole (1) with commercially available 1,3-dibromopropene (*Z*/*E* ratio, 2/1) in the presence of *t*-BuOK and 18-crown-6 led to the vinyl bromides **7a** in 88% yield as a mixture (*Z*/*E*, 2/1) after chromatographic purification. When the mixture **7a** was treated with *n*-$Bu_3SnH$ (1.2 equiv, ca. 0.02 M) in benzene solution with intermittent addition of AIBN over 12 h, the dihydropyrroloindole **13** (24%) and uncyclized product *N*-allylindole **24** (11%) were isolated after chromatography. In an effort to increase both the yield and the ratio of cyclized to uncyclized product, the reaction was repeated, using an initial concentration of substrate of 0.015 M and slow addition of *n*-$Bu_3SnH$ and AIBN over 6 h. Again, the ratio **13**/**24** was ca. 2.5/1 and the isolated yield of **13** was only 27%. Although the use of a mixture of AIBN and ACN (azobis(cyclohexanecarbonitrile)) as initiator did provide improvement, the reaction proved to be erratic in benzene and often incomplete consumption of starting material was observed. The use of toluene proved ameliorative. When a 0.03 M toluene solution of **7a** was heated at reflux with *n*-$Bu_3SnH$/AIBN–ACN for 3 h, amine **13** was isolated in 43% yield after acid extraction. The ratio of cyclized to uncyclized product had increased to 3:1. The use of slow addition of the tin hydride over 1.5–3 h gave the cyclization product **13** in 48–58% yield along with the corresponding reduction product **24** (ca. 20–25%). No attempt was made to isolate other minor products. As expected, no variation in yield or ratio of **13** and **24** was observed when the reaction was conducted on the separated *E* and *Z* isomers.[9] The reaction was less efficient when $Ph_3SnH$, *n*-$Bu_3GeH$,[10] or $(Me_3Si)_3SiH$[11] was used as a reducing agent. Moreover, the Oshima procedure,[12] which employs $Et_3B$/*n*-$Bu_3SnH$ at room temperature, was slower than when the reaction was run with *n*-$Bu_3SnH$ in refluxing toluene; the major product in the former case was *N*-allylindole. When (*E*)-vinyl iodide **7b**, prepared by N-allylation of indole with 3-bromo-1-iodopropene,[13,14] was employed under the optimized conditions mentioned above, the pyrroloindole **13** was obtained in 65% yield. In this case, benzene could be used as solvent without appreciable increase in the reaction time although the reduction product was still present. The products of the reaction mixture were easy to separate because of the basicity of the desired cyclization product.

For examination of the effect of substitution at the 2-position of the indole nucleus on the cyclization, the esters **8** and **9** were examined. In the former instance, the amino ester **14** was obtained in 61% yield along with 17% of the reduction product **25** (Chart I). In the latter case, the esters **9** gave amino ester **15** in 60% yield along with 11% of the reduction product **27**. In both cases, the cyclization product proved to be difficult to extract with acid; separation was achieved by column chromatography. The vinylstannanes **26** and **28** were also isolated from their respective reactions in 3% and 5% yield, respectively. These substances may arise from addition of tri-*n*-butylstannyl radical to *N*-propargylindole, which is formed by elimination of HBr from the vinyl bromide, or alternatively via addition of the tri-*n*-butylstannyl radical to the (*Z*)-olefin bromide with subsequent elimination of bromine atom.[15]

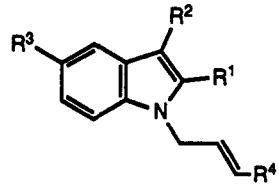
**Table I**

| entry | radical precursors | cyclized products (isolated yield (%)) |
|---|---|---|
| 1 |  **7a** X = Br **7b** X = I (E-isomer) |  **13** (48-58) (65) |
| 2 |  **8** |  **14** (61) |
| 3 |  **9** |  **15** (60) |
| 4 |  **10** |  **16** (55) |
| 5 |  **11a** X = Br **11b** X = I |  **17** (33-42) (31) |
| 6 |  **12** |  **18a** exo (32) **18b** endo (16) |
| 7 |  **33** |  **34** (50) |

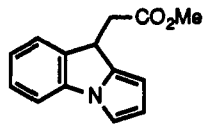
(7) Beckwith, A. L. J.; Westwood, S. W. *Tetrahedron* **1989**, *45*, 5269.
(8) Guida, W. C.; Mathre, D. J. *J. Org. Chem.* **1980**, *45*, 3172.

(9) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.
(10) (a) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578. (b) Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem.* **1986**, *39*, 1151.
(11) Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681.
(12) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron* **1989**, *45*, 923.
(13) 3-Bromo-1-iodopropene was prepared by reaction of (*E*)- or (*Z*)-3-iodo-2-propen-1-ol[14] with $CBr_4$–$PPh_3$/$CH_2Cl_2$ at 0 °C.
(14) (a) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. (b) Feldman, K. S. *Tetrahedron Lett.* **1982**, *23*, 3031.

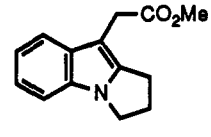
**Chart I**



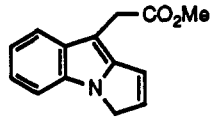
**24** $R^1 = R^2 = R^3 = R^4 = H$
**25** $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$
**26** $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = n\text{-}Bu_3Sn$
**27** $R^1 = CO_2Et$, $R^2 = R^4 = H$, $R^3 = OBn$
**28** $R^1 = CO_2Et$, $R^2 = H$, $R^3 = OBn$, $R^4 = n\text{-}Bu_3Sn$
**29** $R^1 = R^3 = R^4 = H$, $R^2 = CH_2CO_2Me$
**30** $R^1 = R^3 = H$, $R^2 = CH_2CO_2Me$, $R^4 = n\text{-}Bu_3Sn$
**31** $R^1 = R^3 = R^4 = H$, $R^2 = CO_2Me$
**32** $R^1 = R^2 = CO_2Me$, $R^3 = R^4 = H$



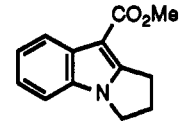
**19**



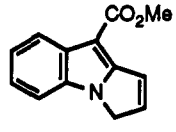
**20**



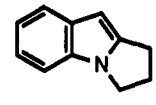
**21**



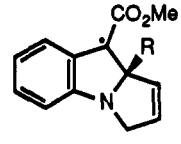
**22**



**23**



**35**



**36a**, R = $CO_2Me$
**b**, R = H

The effect of a 3-alkyl substituent on the indole nucleus was tested with vinyl bromides **10**. In addition to the formation of the dihydropyrroloindole **16** as a 55:45 mixture of undetermined stereochemistry and the reduction product **29** (12%), the pyrroloindoles **19** and **21**, dihydropyrroloindole **20**, and the vinylstannane **30** were formed in minor amounts. The low selectivity in the formation of **16** was surprising because the intermediate radical from cyclization was expected to add a hydrogen atom from the exo face of the dihydropyrroloindole nucleus. While the formation of **19** and **21** can be considered the products of oxidation of the labile dihydropyrroloindole nucleus, the presence of **20** is surprising. Compounds **20** and **21** were isolated as a mixture (6%) and their structures were assigned by comparison of their $^1H$ NMR spectra to the structures of their known lower homologues, **22**[16] and **23**.[17]

In an effort to gain a better understanding of the effect of a substituent at the 3-position of the indole nucleus, the cyclization of esters **11a** was investigated. The behavior of these compounds toward radical cyclization was quite capricious, but after some experimentation, moderate yields (33–42%) of the dihydropyrroloindoles **17** (1:1 mixture) along with 17% of reduction product **31** were obtained. The $^1H$ NMR spectrum of **17** revealed multiplets at $\delta$ 5.14 ($W_{1/2} \sim 10$ Hz) and 5.06 ($W_{1/2} \sim 18$ Hz), which were assigned to the $C_{9a}$-H of the trans and cis isomers, respectively. This assignment is supported by the doublets at $\delta$ 4.33 ($J = 10.6$ Hz) and 4.19 ($J = 4.0$ Hz) corresponding to $C_9$-H of each isomer, which is in accord with coupling constants in related systems.[2,3] The dihydropyrroloindole **22** (4%) and pyrroloindole **23** (9%) were also formed, both of which appeared in the reaction mixture at early conversion. When the mixture of cyclization products **17** was resubjected to the reaction conditions in the presence of *n*-$Bu_3SnH$ for 2 h, the isomer **22** was isolated in 10% yield. In a control experiment, esters **17** were unaffected by *n*-$Bu_3SnBr$ or *n*-$Bu_3SnI$ in refluxing toluene. When the vinyl iodides **11b** were employed in refluxing benzene solution, the yield of **17** was slightly lower than that obtained with the bromides **11a**, but **23** could not be detected in the crude reaction mixture by $^1H$ NMR. If halogen atom transfer were operating in the case of the iodide, the formation of **23** would be expected to be significant. The formation of **22** can be viewed as arising from isomerization of the allylic amine residue of **17** to its enamine and then isomerization to **22**. The allylic isomerization can arise by abstraction of the allylic methine hydrogen by tri-*n*-butylstannyl radical followed by redonation of a hydrogen atom to generate the enamine. When **23** was subjected to standard hydrogenation conditions (1 atm $H_2$, 10% Pd/C, EtOAc), **22** was obtained in quantitative yield.

In an effort to test the effect of substituents at both the 2- and 3-positions of the indole nucleus, the indole-2,3-dicarboxylate derivatives **12** were prepared. When these bromides were subjected to the radical cyclization conditions, the products (isolated yields) **18a** (31%), **18b** (16%), **23** (12%), and **32** (16%) were formed. The stereochemistry of the major diester **18a** was assigned by inference as having the exo stereochemistry. The presence of the 2-carbomethoxy group should hinder hydrogen atom abstraction from the exo face of the intermediate radical **36a** from cyclization relative to the radical **36b** derived from cyclization of the 2-unsubstituted substrate **11**. On the other hand, the endo face of both radicals should be equivalent. The formation of monoester **23** was surprising. While no experiments were conducted to elucidate the mechanism of its formation, the loss of carbomethoxy radical from **36a** is a possibility.

A radical generated at an $sp^3$ center was examined to test further the nature of this cyclization. The success of this process was in doubt because alkyl radicals are less reactive than vinyl radicals.[4,18] The *N*-iodide **33** was prepared in unoptimized yield by the alkylation of indole with 1,3-diiodopropane. Cyclization of **33** gave the known[19a] tetrahydropyrroloindole **34** in 50% yield along

(15) The latter suggestion was offered by a referee.

(16) Nakatsuka, S.; Asano, O.; Goto, T. *Chem. Lett.* **1987**, 1225.
(17) The corresponding ethyl ester is known: Franck, R. W.; Bernady, K. F. *J. Org. Chem.* **1968**, *33*, 3050.
(18) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877.

with significant amounts of the reduction product *N*-propylindole[20] (26%) and the dihydropyrroloindole **35**[19] (10%). The latter compound may arise via halogen transfer because its yield increased at the expense of **34** when the reaction was repeated using slow addition of the tin hydride over a prolonged time.

The moderate yields obtained in these reactions are in accord with the observations of Beckwith,[7] who has shown that, in the case of the intramolecular cyclization of 4-aza-6-(methoxycarbonyl)-5-hexenyl radicals, the direct attachment of a nitrogen atom to the double bond changes the electronic nature of the alkene, making such cyclizations less efficient than the all-carbon analogue. In the case of the indole ring the expected lower reactivity of the 2,3-double bond, compared with the cases studied by Beckwith, would make the effect more noticeably.

In conclusion, this work demonstrates that vinyl radicals are able to react in an intramolecular fashion with the 2,3-double bond of indoles to permit a new entry to the dihydro(tetrahydro)pyrroloindole nucleus. Even though the yields are variable, the simplicity of the scheme provides an attractive alternative to other methods.

## Experimental Section

HPLC: Du Pont Zorbax, 4.6 × 250 mm, 5 μm, 2.0 mL/min, 20% EtOAc/heptane. All reactions were carried out under a positive pressure of $N_2$. Tetrahydrofuran (THF), ethyl ether ($Et_2O$), toluene, and benzene were distilled immediately before use from sodium benzophenone ketyl. The methyl esters of the commercial indolecarboxylic acids were prepared by treatment of the indolecarboxylic acids with diazomethane.

**General Procedure for the Preparation of the Vinyl Halides. (*E*)- and (*Z*)-1-(3-Bromo-2-propenyl)-1*H*-indole (7a).** To a solution of 18-crown-6 (0.80 g, 3.0 mmol) in dry $Et_2O$ (50 mL) was added *t*-BuOK (4.90 g, 35 mmol) at room temperature under nitrogen. To the stirred mixture was added indole (3.50 g, 30 mmol) in a single portion. After 15 min, the reaction mixture was cooled to 0 °C and a solution of 1,3-dibromopropene (7.0 g, 35 mmol) in $Et_2O$ (20 mL) was added dropwise over a 5-min period. After the addition was completed, the cooling bath was removed and the reaction mixture was stirred for 2 h at room temperature. Water (50 mL) was added, the layers were separated, and the aqueous phase was extracted with $Et_2O$ (3 × 20 mL). The combined organic solution was washed with brine (1 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Flash chromatography of the residual dark liquid gave a 2:1 mixture of **7a(Z)** and **7a(E)** (6.23 g, 88%) as a pale yellow oil. Rechromatography of a portion of this mixture using hexane–ethyl acetate (15:1) as eluent provided pure samples of the less polar isomer **7a(Z)** and the more polar isomer **7a(Z)** as pale yellow oils. Isomer **7a(Z)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 7.66 (dt, 1 H, *J* = 7.9, 1.0 Hz, Ar), 7.37 (dd, 1 H, *J* = 8.1, 0.9 Hz, Ar), 7.28–7.11 (m, 2 H, Ar), 7.13 (d, 1 H, *J* = 3.2 Hz, Ar), 6.54 (dd, 1 H, *J* = 3.2, 0.9 Hz, Ar), 6.42 (dt, 1 H, *J* = 7.2, 1.6 Hz, CH=C*H*Br), 6.30 (dt, 1 H, *J* = 7.2, 6.0 Hz, C*H*=CHBr), 4.92 (dd, 2 H, *J* = 6.0, 1.6 Hz, $NCH_2$); EIMS (20 eV) *m/z* 237 (100), 235 (91), 156 (90), 155 (16), 154 (27), 130 (30), 129 (33), 128 (14), 116 (10); EIHRMS calcd for $C_{11}H_{10}BrN$ 236.9976, found 236.9971. Anal. Calcd for $C_{11}H_{10}BrN$: C, 55.96; H, 4.27; N, 5.93. Found: C, 55.78; H, 4.25; N, 5.86. Isomer **7a(E)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 7.66 (dt, 1 H, *J* = 7.8, 1.0 Hz, Ar), 7.32–7.11 (m, 3 H, Ar), 7.06 (d, 1 H, *J* = 3.2 Hz, Ar), 6.55 (dd, 1 H, *J* = 3.2, 0.8 Hz, Ar), 6.37 (dt, 1 H, *J* = 13.6, 5.7 Hz, C*H*=CHBr), 6.11 (dt, 1 H, *J* = 13.6, 1.6 Hz, CH=C*H*Br), 4.68 (dd, 2 H, *J* = 5.7, 1.6 Hz, $NCH_2$); EIMS (20 eV) *m/z* 237 (43), 235 (42), 156 (100), 155 (15), 154 (24), 130 (20), 129 (26), 128 (13), 116 (8); EIHRMS calcd for $C_{11}H_{10}BrN$ 236.9976, found 236.9989. Anal. Calcd for $C_{11}H_{10}BrN$: C, 55.96; H, 4.27; N, 5.93. Found: C, 55.54; H, 4.23; N, 5.53.

**(*E*)-1-(3-Iodo-2-propenyl)-1*H*-indole (7b).** The procedure employed for the preparation of **7a** was followed with indole (0.242 g, 2.06 mmol), *t*-BuOK (0.255 g, 2.27 mmol), 18-crown-6 (0.055 g, 0.20 mmol), and (*E*)-3-bromo-1-iodopropene[13] (0.510 g, 2.06 mmol) in $Et_2O$ (15 mL). The brown oil obtained after workup was chromatographed, using hexane–ethyl acetate (19:1), to give the impure product as a yellow oil. Rechromatography with hexane–ethyl acetate (49:1) yielded the unstable **7b** (0.298 g, 51%) as a pale yellow oil: $^1$H NMR (250 MHz) δ 7.68 (dt, 1 H, *J* = 7.7, 1.0 Hz, Ar), 7.33–7.13 (m, 3 H, Ar), 7.08 (d, 1 H, *J* = 3.2 Hz, H-2), 6.71 (dt, 1 H, *J* = 14.5, 5.4 Hz, C*H*=CHI), 6.57 (dd, 1 H, *J* = 3.2, 0.7 Hz, H-3), 6.15 (dt, 1 H, *J* = 14.5, 1.6 Hz, CH=C*H*I), 4.69 (dd, 2 H, *J* = 5.4, 1.6 Hz, $NCH_2$); EIHRMS calcd for $C_{11}H_{10}IN$ 282.9858; found 282.9849.

**Methyl (*E*)- and (*Z*)-1-(3-Bromo-2-propenyl)-1*H*-indole-2-carboxylate (8).** The procedure used for the preparation of **7a** was followed. The reaction was performed with methyl indole-2-carboxylate (1.42 g, 8.1 mmol), *t*-BuOK (1.09 g, 9.7 mmol), 18-crown-6 (0.21 g, 0.81 mmol), and 1,3-dibromopropene (1.94 g, 9.72 mmol) in 20 mL of $Et_2O$. After workup, a yellow oil was obtained (2.3 g). Column chromatography of this crude mixture using hexane–ethyl acetate (19:1) as eluent gave a diastereomeric mixture **8** (*Z*/*E*, ca. 2:1) (2.06 g, 86%) as a pale yellow solid. Rechromatography of a portion of this mixture using hexane–ethyl acetate (9:1) as eluent provided samples of the less polar isomer **8(Z)** and the more polar isomer **8(E)**. Isomer **8(Z)**: obtained as an off-white solid after recrystallization from hexanes at −22 °C; mp 62–63 *C*; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.70 (dt, 1 H, *J* = 8.0, 0.9 Hz, Ar), 7.50–7.34 (m, 2 H, Ar), 7.35 (s, 1 H, Ar), 7.19 (ddd, 1 H, *J* = 8.0, 6.9, 1.1 Hz, Ar), 6.35 (dt, 1 H, *J* = 7.2, 1.6 Hz, CH=C*H*Br), 6.26 (dt, 1 H, *J* = 7.2, 5.6 Hz, C*H*=CHBr), 5.40 (dd, 2 H, *J* = 5.6, 1.6 Hz, $NCH_2$), 3.94 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1708 $cm^{-1}$; EIHRMS calcd for $C_{13}H_{12}BrNO_2$ 295.0031, found 295.0033. Anal. Calcd for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76. Found: C, 53.15; H, 4.12; N, 4.82. Isomer **8(E)**: obtained as a colorless glass: $^1$H NMR (250 MHz, $CDCl_3$) δ 8.23–8.17 (m, 1 H, Ar), 7.81 (s, 1 H, Ar), 7.34–7.28 (m, 3 H, Ar), 6.40 (dt, 1 H, *J* = 13.7, 5.7 Hz, C*H*=CHBr), 6.25 (dt, 1 H, *J* = 13.7, 1.3 Hz, CH=C*H*Br), 4.73 (dd, 2 H, *J* = 5.7, 1.3 Hz, $NCH_2$), 3.93 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1708 $cm^{-1}$; EIHRMS calcd for $C_{13}H_{12}BrNO_2$ 295.0031, found 295.0027.

**Ethyl 5-(Benzyloxy)-1-(3-bromo-2-propenyl)-1*H*-indole-2-carboxylate (9).** The reaction was carried out with ethyl 5-(benzyloxy)indole-2-carboxylate (2.28 g, 7.72 mmol, dissolved in 10 mL of THF), *t*-BuOK (0.955 g, 8.51 mmol), 18-crown-6 (0.205 g, 0.77 mmol), and 1,3-dibromopropene (1.70 g, 8.51 mmol) in 50 mL of $Et_2O$. After workup, a yellow solid was obtained (3.1 g). Chromatography of the crude mixture using hexane–ethyl acetate (4:1) as eluent yielded the diastereomeric mixture **9** (*Z*/*E*, ca. 2:1) as a light yellow oil, which solidified on standing (2.61 g, 81.5%). Recrystallization from ethanol afforded pale yellow needles (*Z*/*E*, ca. 1.5:1), mp 87–92 °C: $^1$H NMR (250 MHz, $CDCl_3$) δ 7.48–7.08 (m, 18 H, Ar, *Z* and *E*), 6.41–6.20 (m, 3 H, C*H*=CHBr, *Z* and *E* and CH=C*H*Br, *Z*), 6.09 (br dt, 1 H, *J* = 13.6, 1.4 Hz, CH=C*H*Br, *E*), 5.34 (dd, 2 H, *J* = 5.5, 1.4 Hz, $NCH_2$, *Z*), 5.14 (dd, 2 H, *J* = 5.8, 1.4 Hz, $NCH_2$, *E*), 5.09 (s, 4 H, $OCH_2Ph$, *Z* and *E*), 4.38 (q, 2 H, *J* = 7.1 Hz, $CH_2CH_3$, *Z*), 4.36 (q, 2 H, *J* = 7.1 Hz, $CH_2CH_3$, *E*), 1.40 (t, 6 H, *J* = 7.1 Hz, $CH_3$, *Z* and *E*); IR ($CCl_4$) 1708 $cm^{-1}$; EIMS (20 eV) *m/z* 415 (61), 413 (58), 334 (8), 324 (100), 322 (96), 243 (16), 214 (7), 170 (18), 121 (13), 119 (11), 91 (17); EIHRMS calcd for $C_{21}H_{20}BrNO_3$ 415.0606, found 415.0581. Anal. Calcd for $C_{21}H_{20}BrNO_3$: C, 60.88; H, 4.87; N, 3.38. Found: C, 60.77; H, 4.88; N, 3.37.

**Methyl [1-(3-Bromo-2-propenyl)-1*H*-indol-3-yl]acetate (10).** The procedure for the preparation of **9** was followed. The reaction was run with methyl 3-indolylacetate (2.03 g, 10.73 mmol), *t*-BuOK (1.325 g, 11.80 mmol), 18-crown-6 (0.284 g, 1.07 mmol), and 1,3-dibromopropene (2.58 g, 12.88 mmol). After workup, a brown oil was obtained. Chromatography of the crude mixture using hexane–ethyl acetate (9:1) as eluent gave the unstable bromide **10** (*Z*/*E*, ca. 2:1) as a light yellow oil (2.38 g, 72%): $^1$H NMR (250 MHz, $CDCl_3$) δ 7.60 (d, 2 H, *J* = 7.7 Hz, Ar, *Z* and *E*), 7.33–7.05 (m, 8 H, Ar, *Z* and *E*), 6.39 (dt, 1 H, *J* = 7.1, 1.6 Hz, CH=C*H*Br, *Z*), 6.36–6.23 (m, 2 H, C*H*=CHBr, *Z* and *E*), 6.14 (dt, 1 H, *J* = 13.6, 1.5 Hz, CH=C*H*Br, *E*), 4.85 (dd, 2 H, *J* = 6.1, 1.6 Hz, $NCH_2$, *Z*), 4.64 (dd, 2 H, *J* = 5.7, 1.5 Hz, $NCH_2$, *E*), 3.76

(19) (a) Laschtuvka, E.; Huisgen, R. *Chem. Ber.* **1960**, *93*, 81. (b) Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 870.

(20) Cardillo, B.; Casnati, G.; Pochini, A.; Ricca, A. *Tetrahedron* **1967**, *23*, 3771.

(s, 4 H, $CH_2CO_2CH_3$, Z and E), 3.70 (s, 6 H, $OCH_3$, Z and E); IR (film) 1734 $cm^{-1}$; EIMS (20 eV) m/z 309 (43), 307 (48), 250 (94), 248 (100), 168 (74), 121 (13), 119 (12); EIHRMS calcd for $C_{14}H_{14}BrNO_2$ 309.0187, found 309.0164. Anal. Calcd for $C_{14}H_{14}BrNO_2$: C, 54.56; H, 4.58; N, 4.54. Found: C, 54.53; H, 4.61; N, 4.53.

**Methyl (E)- and (Z)-1-(3-Bromo-2-propenyl)-1H-indole-3-carboxylate (11a).** The procedure used for the preparation of **7a** was followed. The reaction was performed with methyl indole-3-carboxylate (2.74 g, 15.6 mmol), t-BuOK (1.94 g, 17.2 mmol), 18-crown-6 (0.414 g, 1.56 mmol), and 1,3-dibromopropene (3.76 g, 18.7 mmol) in 100 mL of $Et_2O$. The indole derivative was added as a solution in 4:1 $Et_2O$–THF (70 mL). After workup, an orange semisolid was obtained (4.62 g). Chromatographic purification of the crude mixture using hexane–ethyl acetate (4:1) as eluent yielded the isomeric mixture **11a** (Z/E, 2:1) (3.87 g, 84%) as pale yellow solid. Rechromatography of a portion of this mixture using hexane–ethyl acetate (9:1) as eluent provided samples of the less polar isomer **11a(Z)** and the more polar isomer **11a(E)** as off-white solids. Isomer **11a(Z)**: recrystallization from hexane at −22 °C gave colorless crystals; mp 41–42 °C; $^1H$ NMR (250 MHz, $CDCl_3$) δ 8.23–8.17 (m, 1 H, Ar), 7.84 (s, 1 H, Ar), 7.41–7.28 (m, 3 H, Ar), 6.50 (dt, 1 H, J = 7.2, 1.7 Hz, CH=C*H*Br), 6.30 (dt, 1 H, J = 7.2, 6.3 Hz, C*H*=CHBr), 4.92 (dd, 2 H, J = 6.3, 1.7 Hz, $NCH_2$), 3.93 (s, 3 H, $OCH_3$); IR (film) 1700 $cm^{-1}$; EIMS (20 eV) m/z 295 (87), 293 (88), 264 (45), 262 (42), 182 (37), 154 (100); EIHRMS calcd for $C_{13}H_{12}BrNO_2$ 295.0031, found 295.0021. Anal. Calcd for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76. Found: C, 53.13; H, 4.09; N, 4.81. Isomer **11a(E)**: contaminated with ca. 10% of another product, presumably the acetylenic compound; mp 115–120 °C; $^1H$ NMR (250 MHz, $CDCl_3$ δ 8.23–8.17 (m, 1 H, Ar), 7.81 (s, 1 H, Ar), 7.34–7.28 (m, 3 H, Ar), 6.40 (dt, 1 H, J = 13.7, 5.7 Hz, C*H*=CHBr), 6.25 (dt, 1 H, J = 13.7, 1.3 Hz, CH=C*H*Br), 4.73 (dd, 2 H, J = 5.7, 1.3 Hz, $NCH_2$), 3.93 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1702 $cm^{-1}$; EIHRMS calcd for $C_{13}H_{12}BrNO_2$ 295.0031, found 295.0024.

**Methyl (E)- and (Z)-1-(3-Iodo-2-propenyl)-1H-indole-3-carboxylate (11b).** The procedure employed for the preparation of **11a** was followed. The reaction was carried out with methyl indole-3-carboxylate (1.02 g, 5.82 mmol), t-BuOK (0.720 g, 6.41 mmol), 18-crown-6 (0.154 g, 0.58 mmol), and 3-bromo-1-iodopropene[13] (1.730 g, 7.0 mmol) in $Et_2O$ (40 mL). The ester was added as a solution in 4:1 $Et_2O$–THF (50 mL). The oil obtained after workup was chromatographed, using hexane–ethyl acetate (17:3), to give first pure **11b(Z)** (0.244 g, 12%), then a 1:1 mixture of cis and trans isomers (0.219 g, 11%), and finally pure **11b(E)** (1.136 g, 57%). Isomer **11b(Z)**: obtained as a pale yellow glass; $^1H$ NMR (250 MHz) δ 8.22–8.18 (m, 1 H, Ar), 7.85 (s, 1 H, H-2), 7.39–7.28 (m, 3 H, Ar), 6.64 (dt, 1 H, J = 7.7, 1.6 Hz, CH=C*H*I), 6.43 (dt, 1 H, J = 7.7, 6.0 Hz, C*H*=CHI), 4.86 (dd, 2 H, J = 6.0, 1.6 Hz, $NCH_2$), 3.92 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1701 $cm^{-1}$; EIHRMS calcd for $C_{13}H_{12}INO_2$ 340.9913, found 340.9901. Isomer **11b(E)**: obtained as white crystals after recrystallization from hexane–$CH_2Cl_2$; mp 112–114 °C; $^1H$ NMR (250 MHz) δ 8.23–8.18 (m, 1 H, Ar), 7.80 (s, 1 H, H-2), 7.33–7.28 (m, 3 H, Ar), 6.70 (dt, 1 H, J = 14.6, 5.7 Hz, C*H*=CHI), 6.27 (dt, 1 H, J = 14.6, 1.6 Hz, CH=C*H*I), 4.70 (dd, 2 H, J = 5.7, 1.6 Hz, $NCH_2$), 3.93 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1700 $cm^{-1}$; EIHRMS calcd for $C_{13}H_{12}INO_2$ 340.9913, found 340.9904.

**Dimethyl (E)- and (Z)-1-(3-Bromo-2-propenyl)-1H-indole-2,3-dicarboxylate (12).** The reaction was performed with the dimethyl 1H-indole-2,3-dicarboxylate[21] (1.10 g, 4.72 mmol), t-BuOK (0.62 g, 5.52 mmol), 18-crown-6 (0.145 g, 0.55 mmol), and 1,3-dibromopropene (1.11 g, 5.52 mmol) in 18 mL of $Et_2O$. After workup, a yellow solid was obtained (1.5 g). Chromatographic purification of the crude product (hexane–ethyl acetate, 4:1) gave **12** as a mixture of diastereomers (1.36 g, 82%). HPLC analysis showed a 2:1 ratio of Z ($t_R$ 15.07 min) to E ($t_R$ 17.24 min) isomers. Careful rechromatography of a portion of this mixture using benzene–ethyl acetate (99:1) as eluent provided samples of the less polar isomer **12(Z)** and the more polar isomer **12(E)**. Isomer **12(Z)**: obtained as a crystalline, off-white solid after recrystallization from hexane at −22 °C; mp 67–69 °C; $^1H$ NMR (250 MHz, $CDCl_3$) δ 8.13 (dt, 1 H, J = 8.0, 1.0 Hz, Ar), 7.45–7.29 (m, 3 H, Ar), 6.42 (dt, 1 H, J = 7.2, 1.8 Hz, CH=C*H*Br), 6.26 (dt, 1 H, J = 7.2, 6.0 Hz, C*H*=CHBr), 5.03 (dd, 2 H, J = 6.0, 1.8 Hz, $NCH_2$), 4.03 (s, 3 H, $OCH_3$), 3.94 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1719 (shoulder), 1708 $cm^{-1}$; EIHRMS calcd for $C_{15}H_{14}BrNO_4$ 353.0086, found 353.0075. Anal. Calcd for $C_{15}H_{14}BrNO_4$: C, 51.16; H, 4.01; N, 3.98. Found: C, 51.23; H, 4.12; N, 3.89. Isomer **12(E)**: obtained as a glass; $^1H$ NMR (250 MHz, $CDCl_3$) δ 8.12 (dt, 1 H, J = 7.6, 1.2 Hz, Ar), 7.40–7.28 (m, 3 H, Ar), 6.35 (dt, 1 H, J = 13.7, 5.6 Hz, C*H*=CHBr), 6.23 (dt, 1 H, J = 13.7, 1.0 Hz, CH=C*H*Br), 4.86 (dd, 2 H, J = 5.6, 1.0 Hz, $NCH_2$), 4.01 (s, 3 H, $OCH_3$), 3.94 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1719 (shoulder), 1708 $cm^{-1}$; EIHRMS calcd for $C_{15}H_{14}BrNO_4$ 353.0086, found 353.0069.

**1-(3-Iodopropyl)-1H-indole (33).** The general procedure was followed, using indole (2.27 g, 19.37 mmol), t-BuOK (2.39 g, 21.29 mmol), 18-crown-6 (0.51 g, 1.93 mmol), and 1,3-diiodopropane (11.45 g, 38.7 mmol). After 18 h, the reaction was worked up. $^1H$ NMR analysis of the crude mixture showed the presence of the desired product along with N-allylindole[8,20] (**24**) and 50% of starting material. Chromatography using hexane–ethyl acetate (10:1) provided **33** (2.23 g) contaminated with **24** and recovered indole (1.21 g). Rechromatography (hexane–ethyl acetate, 20:1) gave first N-allylindole (0.48 g, 16%) and then the pure title compound **33** (1.23 g, 22%) as a colorless oil: $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.63 (dt, 1 H, J = 7.8, 1.0 Hz, Ar), 7.36 (m, 1 H, Ar), 7.21 (ddd, 1 H, J = 8.2, 7.0, 1.2 Hz, Ar), 7.14–7.07 (m, 2 H, Ar), 6.49 (dd, 1 H, J = 3.2, 0.8 Hz, Ar), 4.24 (t, 2 H, J = 6.4 Hz, $NCH_2CH_2$), 3.04 (t, 2 H, J = 6.5 Hz, $CH_2CH_2I$), 2.28 (pent., 2 H, J = 6.4 Hz, $CH_2CH_2CH_2$); EIMS (20 eV) m/z 285 (48), 158 (6), 130 (100); EIHRMS calcd for $C_{11}H_{12}IN$ 285.0015, found 285.0021. Anal. Calcd for $C_{11}H_{12}IN$: C, 46.34; H, 4.24; N, 4.91. Found: C, 46.11; H, 4.26; N, 4.87.

**Radical Cyclization of 7a. 9,9a-Dihydro-3H-pyrrolo[1,2-a]indole (13).** A degassed solution of the bromide **7a** (Z/E, ca. 2:1) (0.237 g, 1.0 mmol) and 1,1′-azobis(cyclohexanecarbonitrile) (ACN) (0.013 g, 0.05 mmol) in dry toluene (65 mL) was heated to reflux, using a 250-W sunlamp. A solution of n-$Bu_3SnH$ (0.350 g, 1.2 mmol) and AIBN (0.009 g, 0.05 mmol) in toluene (2 mL) was added to the stirred solution of **7a** over 1.5 h, using a syringe pump. After 1 h of additional refluxing, $^1H$ NMR analysis indicated that all of the starting material had been consumed and a ca. 3:1 ratio of cyclized to uncyclized product had been formed. The mixture was heated at reflux for an additional 30 min period and the solvent was then evaporated under reduced pressure. The residue was dissolved in ethyl ether (20 mL) and extracted with a cold 0.5 M HCl solution (5 × 10 mL). The acid aqueous solution was washed with ether (1 × 10 mL) and recooled, and then the pH was adjusted to 10 by the addition of 2 M NaOH solution. This mixture was extracted with $CH_2Cl_2$ (5 × 10 mL), and the combined organic layer was dried ($MgSO_4$) and concentrated to give **13** (0.088 g, 56%) as a pale yellow oil. Flash chromatography (hexane–ethyl acetate, 4:1) afforded pure **13** (0.075 g, 48%) as a colorless oil that darkened on standing: $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.18–7.10 (m, 2 H, H-5 and H-7), 6.84 (ddd, 1 H, J = 7.4, 7.4, 0.8 Hz, H-6), 6.77 (d, 1 H, J = 7.8 Hz, H-8), 5.83 (d, 2 H, AB system, H-1 and H-2), 4.88–4.78 (m, 1 H, H-9a), 4.13 (ddd, 1 H, J = 15.0, 4.3, 1.1 Hz, H-3), 3.96 (dd, 1 H, J = 15.0, 3.6 Hz, H-3′), 3.28 (dd, 1 H, J = 16.0, 10.1 Hz, H-9), 3.11 (dd, 1 H, J = 16.0, 4.0 Hz, H-9′); $^{13}C$ NMR ($CDCl_3$) δ 155.1 (s, Ar), 132.0 (C-1 or C-2), 129.8 (s, Ar), 127.3 (d, Ar), 127.1 (C-1 or C-2), 124.6 (d, Ar), 120.3 (d, Ar), 112.3 (d, Ar), 70.5 (C-9a), 60.9 (C-3), 33.8 (C-9); EIMS (20 eV) m/z 157 (23), 156 (100), 155 (15), 129 (18); CIHRMS calcd for $C_{11}H_{12}N$ (M + H) 158.0970, found 158.0981. Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.68; H, 6.89; N, 8.73. The ethereal extract containing the neutral reaction products was washed with brine and treated with saturated KF solution (20 mL). After 1 h, the mixture was filtered through Celite, the layers were separated, and the aqueous solution was extracted with ethyl ether (2 × 10 mL). The combined organic extracts were dried and concentrated. Flash chromatography (stepwise gradient of hexane and hexane–ethyl acetate, 10:1) of the residue gave N-allylindole[8,20] (**24**) as a colorless oil (0.033 g, 21%).

**Radical Cyclization of 8.** The procedure used for the preparation of **13** was followed. To a refluxing solution of the bromide **8** (Z/E, ca. 2:1) (0.268 g, 0.911 mmol) and ACN (0.015

(21) Diels, O.; Reese, J. *Ann.* **1934**, *511*, 168.

g, 0.06 mmol) in toluene (28 mL) was added a solution of *n*-$Bu_3SnH$ (0.400 g, 1.37 mmol), AIBN (0.008 g, 0.046 mmol), and ACN (0.006 g, 0.025 mmol) in toluene (2 mL) over 1.5 h, via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 4 h with the concomitant addition of more AIBN (0.010 g) in toluene (1 mL). Evaporation of the solvent under reduced pressure furnished a yellow oil. TLC (hexane–ethyl acetate, 4:1) analysis of the crude material showed the presence of three main products and the $^1H$ NMR spectrum indicated a ca. 3.7:1 ratio of cyclized to uncyclized products. Flash chromatography (stepwise gradient of hexane, hexane–ethyl acetate, 10:1 and 4:1) of this mixture gave the less polar tin addition product **26** (0.012 g, 3%), then the reduction product **25** (0.032 g, 17%), and finally the more polar compound **14** (0.119 g, 61%).

**Methyl 1-[(*E*)-3-(Tri-*n*-butylstannyl)-2-propenyl]-1*H*-indole-2-carboxylate (26).** Colorless oil. No correct elemental analysis could be obtained for this compound owing to the contamination with a small amount of organotin derivatives. **26**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.69 (dt, 1 H, $J$ = 8.0, 1.0 Hz, Ar), 7.39–7.28 (m, 3 H, Ar), 7.15 (ddd, 1 H, $J$ = 8.0, 6.4, 1.6 Hz, Ar), 6.08 (dt, 1 H, $J$ = 19.0, 4.5 Hz, C*H*=CHSn), 5.84 (dt, 1 H, $J$ = 19.0, 1.6 Hz, CH=C*H*Sn), 5.28 (dd, 2 H, $J$ = 4.5, 1.6 Hz, $NCH_2$), 3.90 (s, 3 H, $OCH_3$), 1.56–1.35 (m, 6 H), 1.34–1.19 (m, 6 H), 0.91–0.81 (m, 15 H): IR ($CDCl_3$) 1710 $cm^{-1}$; EIMS (20 eV) $m/z$ 505 (1.2), 504 (1.4), 452 (3.5), 451 (15), 449 (116), 448 (21), 447 (100), 446 (39), 445 (67), 444 (28), 443 (38), 391 (11), 389 (8), 293 (8), 291 (6), 264 (8), 262 (6), 335 (5), 214 (5), 184 (26), 179 (7), 177 (7), 168 (21); EIHRMS calcd for $C_{25}H_{39}NO_2Sn$ 505.2003, found 505.2035.

**Methyl 1-(2-propenyl)-1*H*-indole-2-carboxylate (25)**: colorless oil; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.70 (d, 1 H, $J$ = 8.0 Hz, Ar), 7.40–7.31 (m, 3 H, Ar), 7.17 (ddd, 1 H, $J$ = 8.0, 5.9, 2.0 Hz, Ar), 6.02 (ddt, 1 H, $J$ = 17.1, 10.2, 5.0 Hz, C*H*=$CH_aH_b$), 5.25 (dt, 2 H, $J$ = 5.0, 1.6 Hz, $NCH_2$), 5.12 (ddt, 1 H, $J$ = 10.2, ~1.6, ~1.6 Hz, CH=C*H*$_a$H$_b$), 4.91 (ddt, 1 H, $J$ = 17.1, ~1.6, ~1.6 Hz, CH=CH$_a$*H*$_b$), 3.92 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1710 $cm^{-1}$; EIMS (20 eV) $m/z$ 215 (100), 214 (34), 184 (19), 156 (40), 154 (41); EIHRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0958. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.57; H, 6.14; N, 6.48.

**Methyl 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indole-9a-carboxylate (14)**: colorless oil; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.19–7.07 (m, 2 H, Ar), 6.89–6.79 (m, 2 H, Ar), 5.99–5.88 (m, 2 H, AB system, H-1 and H-2), 4.31 (ddd, 1 H, $J$ = 15.4, 2.6, 1.4 Hz, H-3), 3.98 (dt, 1 H, $J$ = 15.4, 1.9 Hz, H-3′), 3.77 (s, 3 H, OMe), 3.56 (d, 1 H, $J$ = 16.6 Hz, H-9), 3.40 (d, 1 H, $J$ = 16.6 Hz, H-9′); $^{13}C$ NMR ($CDCl_3$) $\delta$ 174.0 (C=O), 154.0 (s, Ar), 131.0 (C-1 or C-2), 129.7 (C-1 or C-2), 128.3 (s, Ar), 127.8 (d, Ar), 124.5 (d, Ar), 121.2 (d, Ar), 112.9 (d, Ar), 83.1 (C-9a), 61.8 (C-3), 52.5 ($OCH_3$), 38.1 (C-9): IR ($CDCl_3$) 1729 $cm^{-1}$; EIMS (20 eV) $m/z$ 215 (9), 156 (100), 129 (9); EIHRMS calcd for $C_{13}H_{12}NO_2$ 215.0946, found 215.0964. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.47; H, 6.10; N, 6.50.

**Radical Cyclization of 9.** To a refluxing solution of the bromide **9** (*Z*/*E*, 2:1) (0.300 g, 0.724 mmol), *n*-$Bu_3SnH$ (0.233 g, 0.796 mmol) and ACN (0.015 g, 0.061 mmol) in toluene (28 mL) was added a solution of AIBN (0.015 g, 0.09 mmol) in toluene (1 mL) over 2 h, via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 1 h. Evaporation of the solvent under reduced pressure furnished a yellow oil. TLC (hexane–ethyl acetate, 4:1) analysis of the crude material showed the presence of three main spots and its $^1H$ NMR spectrum indicated a ca. 4:1 ratio of cyclized to uncyclized products. The residue was dissolved in 20 mL of $Et_2O$ and treated with saturated KF solution (10 mL). After 1 h, the mixture was filtered through Celite, the layers were separated, and the aqueous solution was extracted with ethyl ether (3 × 20 mL). The combined organic solution was dried ($MgSO_4$) and concentrated. Flash chromatography (stepwise gradient of hexane–ethyl acetate, 9:1 and 4:1) of the residue gave first the tin derivative **28** (0.025 g, 5%), then the reduction product **27** (0.026 g, 11%), and finally the desired compound **15** (0.146 g, 60%).

**Ethyl 5-(Benzyloxy)-1-[(*E*)-3-(tri-*n*-butylstannyl)-2-propenyl]-1*H*-indole-2-carboxylate (28).** Rechromatography (hexane–ethyl acetate, 98:2) yielded impure **28** as a colorless oil. No correct elemental analysis could be obtained for this compound, owing to contamination with a small amount of other organotin derivatives. **28**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.51–7.24 (m, 7 H, Ar), 7.16 (d, 1 H, $J$ = 2.3 Hz, Ar), 7.08 (dd, 1 H, $J$ = 9.0, 2.5 Hz, Ar), 6.07 (dt, 1 H, $J$ = 19.0, 4.5 Hz, C*H*=CHSn), 5.83 (dt, 1 H, $J$ = 19.0, 1.5 Hz, CH=C*H*Sn), 5.24 (dd, 2 H, $J$ = 4.5, 1.5 Hz, $NCH_2$), 5.11 (s, 2 H, $OCH_2Ph$), 4.36 (q, 2 H, $J$ = 7.1 Hz, $OCH_2CH_3$), 1.46–1.36 (m, 9 H, centered at $\delta$ 1.40 there is a triplet with $J$ = 7.1 Hz corresponding to $OCH_2CH_3$), 1.32–1.17 (m, 6 H), 0.87–0.79 (m, 15 H); IR ($CDCl_3$) 1703 $cm^{-1}$; EIMS (20 eV) $m/z$ 625 (12), 624 (6), 623 (9), 573 (5), 572 (16), 571 (5), 570 (19), 569 (30), 568 (100), 567 (48), 566 (78), 565 (34), 564 (40); EIHRMS calcd for $C_{33}H_{47}NO_3Sn$ 625.2578, found 625.2564.

**Ethyl 5-(Benzyloxy)-1-(2-propenyl)-1*H*-indole-2-carboxylate (27)** was obtained as an off-white solid. After recrystallization from hexane, the product gave the following: mp 89.5–90.5 °C; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.51–7.25 (m, 7 H, Ar), 7.16 (d, 1 H, $J$ = 2.3 Hz, Ar), 7.11 (dd, 1 H, $J$ = 8.9, 2.4 Hz, Ar), 6.00 (ddt, 1 H, $J$ = 17.1, 10.2, 5.0 Hz, C*H*=$CH_aH_b$), 5.21 (dt, 2 H, $J$ = 5.0, 1.5 Hz, $NCH_2$), 5.12 (s, 2 H, $OCH_2Ph$), 5.11 (ddt, 1 H, $J$ = 10.2, ~1.5, ~1.5 Hz, CH=C*H*$_a$H$_b$), 4.91 (ddt, 1 H, $J$ = 17.1, ~1.5, ~1.5 Hz, CH=CH$_a$*H*$_b$), 4.37 (q, 2 H, $J$ = 7.1 Hz, $OCH_2CH_3$), 1.41 (t, 3 H, $J$ = 7.1 Hz, $OCH_2CH_3$); IR ($CDCl_3$) 1703 $cm^{-1}$; EIMS (20 eV) $m/z$ 335 (61), 244 (100), 216 (9), 158 (7); EIHRMS calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1520. Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.25; H, 6.27; N, 4.12.

**Ethyl 7-(benzyloxy)-9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]-indole-9a-carboxylate (15)**: pale yellow solid; recrystallization from ethanol yielded off-white crystals; mp 85–86 °C; $^1H$ NMR (490 MHz, $CDCl_3$) $\delta$ 7.43–7.30 (m, 5 H, Ar), 6.81–6.71 (m, 3 H, Ar), 5.95 (ddd, 1 H, $J$ = 5.8, 2.0, 1.5 Hz), 5.88 (ddd, 1 H, $J$ = 5.8, 2.7, 2.0 Hz), 5.00 (s, 2 H, $OCH_2Ph$), 4.29 (ddd, 1 H, $J$ = 15.4, 2.7, 1.5 Hz, H-3), 4.28–4.18 (m, 2 H, $OCH_2CH_3$), 3.91 (ddd, 1 H, $J$ = 15.4, 2.0, 2.0 Hz, H-3′), 3.53 (d, 1 H, $J$ = 16.6 Hz, H-9), 3.36 (d, 1 H, $J$ = 16.6 Hz, H-9′), 1.30 (t, 3 H, $J$ = 7.1 Hz, $OCH_2CH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 173.5 (C=O), 154.2 (s, Ar), 148.2 (s, Ar), 137.4 (s, Ar), 131.0 (C-1 or C-2), 129.5 (s, Ar), 129.4 (C-1 or C-2), 128.4 (d, 2 C, Ar), 127.7 (d, Ar), 127.3 (d, 2 C, Ar), 114.3 (d, Ar), 113.3 (d, Ar), 111.7 (d, Ar), 83.8 (C-9a), 70.7 ($OCH_2Ph$), 62.3 and 61.3 (C-3 or $OCH_2CH_3$), 38.4 (C-9), 14.1 ($CH_3$); IR ($CCl_4$) 1731 $cm^{-1}$; EIMS (20 eV) $m/z$ 336 (19), 262 (100), 244 (28), 234 (9), 171 (37), 170 (7), 143 (7), 142 (9), 91 (17); EIHRMS calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1520. Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 74.49; H, 6.39; N, 4.10.

**Radical Cyclization of 10.** The same procedure used for the preparation of **15** was followed with the bromide **10** (*Z*/*E*, 2:1) (0.206 g, 0.668 mmol), *n*-$Bu_3SnH$ (0.214 g, 0.736 mmol), and ACN (0.010 g, 0.041 mmol) in toluene (37 mL). The solution of AIBN (0.015 g, 0.09 mmol) in toluene (1 mL) was added over 3 h. After the addition was completed, the reaction mixture was heated at reflux for an additional 1 h. Evaporation of the solvent under reduced pressure furnished a brown oil. TLC (hexane–ethyl acetate, 4:1) analysis of the crude material showed the presence of three main spots. The more polar desired compound was isolated by acid extraction following the same procedure used for the isolation of **13**. Concentration of the $CH_2Cl_2$ extract gave **16** (0.085 g, 55%) as a pale yellow oil. Flash chromatography (hexane–ethyl acetate, 4:1) of this product afforded pure **16** (0.077 g, 50%) as a colorless oil that darkened on standing.

**Methyl [9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indol-9-yl]acetate (16)** was obtained as a 55:45 mixture of diastereomers ($^1H$ NMR analysis): $^1H$ NMR (490 MHz, $CDCl_3$) $\delta$ 7.18–7.13 (m, 2 H, Ar, both isomers), 7.07 and 7.01 (2 d, 2 H, $J$ = 7.3 Hz, Ar, both isomers), 6.86–6.82 (m, 2 H, Ar, both isomers), 6.76–6.74 (m, 2 H, Ar, both isomers), 5.94–5.81 (m, 4 H, H-1 and H-2, both isomers), 5.02 (m, 1 H, $W_{1/2}$ ~ 14 Hz, H-9a, major isomer), 4.48 (m, 1 H, $W_{1/2}$ ~ 8 Hz, H-9a, minor isomer), [4.14–4.07 (m, 2 H) and 4.00–3.79 (m, 4 H)] ($CH_2N$ and H-9, both isomers), 3.78 (s, 3 H, $OCH_3$, major isomer), 3.75 (s, 3 H, $OCH_3$, minor isomer), 2.83 (dd, 1 H, $J$ = 16.7, 4.8 Hz, C*H*$_a$H$_b$$CO_2CH_3$, major isomer), 2.79 (dd, 1 H, $J$ = 16.5, 5.3 Hz, C*H*$_a$H$_b$$CO_2CH_3$, minor isomer), 2.67 (dd, 1 H, $J$ = 16.5, 9.8 Hz, CH$_a$*H*$_b$$CO_2CH_3$, minor isomer), 2.60 (dd, 1 H, $J$ = 16.7, 10.4 Hz, CH$_a$*H*$_b$$CO_2CH_3$, major isomer); $^{13}C$ NMR ($CDCl_3$) $\delta$ 172.9 (3.6), 172.8 (2.5), 155.0 (3.1), 154.6 (2.7), 132.4 (1.8), 132.0 (3.0), 131.6 (6.3), 129.1 (9.9), 128.3 (9.5), 128.1

(12), 127.8 (9.9), 127.3 (8.5), 124.2 (7.6), 123.6 (10.7), 120.7 (8.9), 120.4 (10.2), 112.8 (8.5), 112.3 (9.0), 78.1 (9), 74.8 (11.6), 61.2 (9.4), 60.9 (7.4), 51.8 (4.2), 51.6 (3.5), 42.9 (8.3), 40.6 (7.2), 40.0 (10.1), 37.2 (10.5); IR ($CDCl_3$) 1733 $cm^{-1}$; EIMS (20 eV) $m/z$ 229 (51), 170 (28), 168 (30), 156 (36), 155 (100), 154 (26); EIHRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1113. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.24; H, 6.62; N, 6.10.

The ethereal extract containing the neutral reaction products was washed with brine, dried ($MgSO_4$), and concentrated. The residue was subjected to flash chromatography (stepwise gradient of hexane–ethyl acetate, 9:1 and 17:3). First to elute was the tin derivative **30** (0.011 g, 3%) and then the pyrroloindole **19** (0.011 g, 7%). Further elution with the second solvent gave the reduction product **29** (0.019 g, 12%), and finally an inseparable mixture of the compounds assumed to be **20** and **21** (0.010 g, 6%).

**Methyl [1-[(*E*)-3-(tri-*n*-butylstannyl)-2-propenyl]-1*H*-indol-3-yl]acetate (30)**: colorless oil that was not fully characterized; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.62 (d, 1 H, $J$ = 7.8 Hz, Ar), 7.32–7.09 (m, 4 H, Ar), 6.10 (centered m, 2 H, $^3J_{Sn-H}$ = 64 Hz, C*H*=C*H*Sn), 4.74 (d, 2.0 H, $J$ = 3.0 Hz, $NCH_2$), 3.79 (s, 2 H, $CH_2CO_2CH_3$), 3.71 (s, 3 H, $OCH_3$), 1.58–1.35 (m, 6 H), 1.35–1.20 (m, 6 H), 0.97–0.80 (m, 15 H).

**Methyl [9*H*-pyrrolo[1,2-*a*]indol-9-yl]acetate (19)**: colorless oil; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.39–7.24 (m, 3 H, Ar), 7.13–7.07 (m, 2 H, Ar), 6.37 (t, 1 H, $J$ = 3.1 Hz, H-2), 6.11 (dt, 1 H, $J$ = 3.3, 1.3 Hz, H-1), 4.44 (t, 1 H, $J$ = 7.5 Hz, H-9), 3.80 (s, 3 H, $OCH_3$), 2.89 (dd, 1 H, $J$ = 16.3, 6.5 Hz, $CH_2CO_2CH_3$), 2.68 (dd, 1 H, $J$ = 16.3, 8.5 Hz, $CH_2CO_2CH_3$); IR ($CDCl_3$) 1735 $cm^{-1}$; EIMS (20 eV) $m/z$ 227 (62), 168 (100), 167 (33), 154 (63); EIHRMS calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0952. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.03; H, 5.69; N, 6.12.

**Methyl [1-(2-propenyl)-1*H*-indol-3-yl]acetate (29)**: colorless oil; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.62 (dt, 1 H, $J$ = 7.8, 1.0 Hz, Ar), 7.34–7.10 (m, 4 H, Ar), 6.00 (ddt, 1 H, $J$ = 17.0, 10.4, 5.4 Hz, C*H*=$CH_aH_b$), 5.22 (ddt, 1 H, $J$ = 10.4, ~1.5, ~1.5 Hz, CH=C$H_aH_b$), 5.13 (ddt, 1 H, $J$ = 17.0, ~1.5, ~1.5 Hz, CH=$CH_aH_b$), 4.71 (dt, 2 H, $J$ = 5.4, 1.5 Hz, $NCH_2$), 3.79 (s, 2 H, $CH_2CO_2CH_3$), 3.72 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1734 $cm^{-1}$; EIMS (20 eV) $m/z$ 229 (55), 170 (100); EIHRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1108. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.30; H, 6.65; N, 6.19.

**Methyl [2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indol-9-yl]acetate (20) and Methyl [3*H*-Pyrrolo[1,2-*a*]indol-9-yl]acetate (21).** Colorless oil. This mixture (**20**/**21**, 3:2) presents the same chromatographic mobility as that of the basic compound **16**. **20**/**21**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.61 (d, 1 H, $J$ = 7.6 Hz) and 7.53 (d, 1 H, $J$ = 8.3 Hz) (Ar, **20** and **21**), 7.33–7.04 (m, 6 H, Ar, **20** and **21**), 6.82 (dt, 1 H, $J$ = 6.0, 2.2 Hz, **21**), 6.53 (dt, 1 H, $J$ = 6.0, 2.1 Hz, **21**), 4.59 (bd t, 2 H, $J$ = 2.1 Hz, H-3, **21**), 4.07 (t, 2 H, $J$ = 7.0 Hz, H-3, **20**), 3.82 and 3.78 (2 s, 4 H, $CH_2CO_2CH_3$, **20** and **21**), 3.70 and 3.68 (2 s, 6 H, $OCH_3$, **20** and **21**), 3.01 (t, 2 H, $J$ = 7.4 Hz, H-1, **20**), 2.63 (pent., 2 H, $J$ = 7.2 Hz, H-2, **20**); IR ($CDCl_3$) 1734 $cm^{-1}$; EIMS (20 eV) $m/z$ 229 (M, 48), 227 (M, 32), 203 (17), 170 (100), 168 (67), 167 (21), 154 (8), 144 (34).

**Radical Cyclization of 11a.** The procedure used for the preparation of **13** was followed. To a refluxing solution of the bromide **11a** (*Z*/*E*, 3:1) (0.435 g, 1.47 mmol) and ACN (0.030 g, 0.12 mmol) in toluene (50 mL) was added a solution of *n*-$Bu_3SnH$ (0.516 g, 1.77 mmol), AIBN (0.030 g, 0.18 mmol), and ACN (0.030 g, 0.12 mmol) in toluene (2 mL) over 2.5 h via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 1 h. Evaporation of the solvent under reduced pressure gave a yellow oil. The more polar, desired compound was isolated by acid extraction following the same procedure used for the isolation of **13**, but using 2 M HCl instead of 0.5 M HCl. Concentration of the $CH_2Cl_2$ extract furnished diastereomeric esters **17** (0.127 g, 40%) as a pale yellow oil. Flash chromatography (hexane–ethyl acetate, 85:15) of this product afforded pure **17** (0.112 g, 35%).

**Methyl 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (17)**: colorless oil (1:1 mixture of diastereomers); $^1H$ NMR (490 MHz, $CDCl_3$) $\delta$ 7.26–7.16 (m, 2 H, Ar, both isomers), 6.89–6.74 (m, 4 H, Ar, both isomers), 5.88–5.85 (m, 2 H, H-1 and H-2, one isomer), 5.83–5.77 (m, 2 H, H-1 and H-2, one isomer), 5.14 (m, 1 H, $W_{1/2}$ ~ 10.0 Hz, H-9a, one isomer), 5.06 (m, 1 H, $W_{1/2}$ ~ 18.0 Hz, H-9a, one isomer), 4.33 (d, 1 H, $J$ = 10.6 Hz, H-9, one isomer), 4.19 (d, 1 H, $J$ = 4.0 Hz, H-9, one isomer), 4.15–4.07 (m, 4 H, H-3, both isomers), 4.00–3.90 (m, 4 H, H-3′, both isomers), 3.76 (s, 3 H, $OCH_3$, one isomer), 3.75 (s, 3 H, $OCH_3$, one isomer); $^{13}C$ NMR ($CDCl_3$) $\delta$ 172.9 (2.7), 171.4 (1.4), 155.2 (1.0), 155.1 (1.9), 130.3 (8.4), 129.1 (8.3), 129.0 (6.3), 128.7 (7.3), 128.4 (6.8), 127.9 (6.4), 127.3 (1.6), 127.1 (3.1), 125.9 (8.1), 125.4 (8.5), 120.9 (9.3), 120.8 (9.1), 113.0 (8.2), 112.7 (8.9), 74.0 (9.2), 73.1 (9.7), 61.3 (7.4), 60.8 (7.0), 52.4 (3.8), 52.0 (8.8), 51.8 (3.9), 50.0 (10.8); IR ($CDCl_3$) 1737 $cm^{-1}$; EIMS (20 eV) $m/z$ 215 (100), 200 (12), 184 (12), 156 (70), 155 (32), 154 (42); EIHRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0964. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.38; H, 6.08; N, 6.46.

The ethereal extract containing the neutral reaction products was washed with brine, dried ($MgSO_4$), and concentrated. The residue was subjected to flash chromatography (stepwise gradient of hexane, hexane–ethyl acetate, 19:1, 9:1, 17:3, and 4:1). First to elute was the presumed tin addition product, which was not characterized, and then the reduction product **31** (0.055 g, 17%). Further elution of the column gave the dihydropyrroloindole **22** (0.012 g, 4%) and finally the pyrroloindole **23** (0.027 g, 9%).

**Methyl 1-(2-propenyl)-1*H*-indole-3-carboxylate (31)** was obtained as an off-white solid. Recrystallization from hexane gave white crystals: mp 45.5–46.5 °C; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 8.22–8.15 (m, 1 H, Ar), 7.80 (s, 1 H, H-2), 7.35–7.22 (m, 3 H, Ar), 5.96 (ddt, 1 H, $J$ = 17.0, 10.4, 5.4 Hz, C*H*=$CH_aH_b$), 5.24 (ddt, 1 H, $J$ = 10.4, ~1.4, ~1.4 Hz, CH=C$H_aH_b$), 5.11 (ddt, 1 H, $J$ = 17.0, ~1.6, -1.6 Hz, CH=$CH_aH_b$), 4.70 (dt, 2 H, $J$ = 5.4, 1.6 Hz, $NCH_2$), 3.90 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1693 $cm^{-1}$; EIMS (20 eV) $m/z$ 215 (100), 200 (8), 184 (78), 156 (46); EIHRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0958. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.51; H, 6.15; N, 6.48.

**Methyl 2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (22).** This neutral compound, obtained as an off-white solid, displayed the same chromatographic mobility as the amine **17**. Recrystallization from 30% ethyl acetate in hexane gave colorless crystals, mp 89.5–90.5 °C (lit.[15] mp 87–88 °C): $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 8.11 (m, 1 H, Ar), 7.28–7.19 (m, 3 H, Ar), 4.10 (t, 2 H, $J$ = 7.2 Hz, H-3), 3.91 (s, 3 H, $OCH_3$), 3.29 (t, 2 H, $J$ = 7.5 Hz, H-1), 2.65 (tt, 2 H, $J$ ~ 7.4, 7.4 Hz, H-2); IR ($CDCl_3$) 1690 $cm^{-1}$; EIMS (20 eV) $m/z$ 215 (100), 200 (30), 184 (96), 156 (27); EIHRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0955.

**Methyl 3*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (23)** was obtained as a light yellow glass: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 8.22–8.15 (m, 1 H, Ar), 7.33–7.20 (m, 3 H, Ar), 7.16 (dt, 1 H, $J$ = 6.0, 2.1 Hz, H-1), 6.79 (dt, 1 H, $J$ = 6.0, 2.0 Hz, H-2), 4.61 (t, 2 H, $J$ = 2.0 Hz, H-3), 3.92 (s, 3 H, $OCH_3$); IR ($CDCl_3$) 1691 cm1–; EIMS (20 eV) $m/z$ 213 (73), 198 (31), 182 (16), 154 (100); EIHRMS calcd for $C_{13}H_{11}NO_2$ 213.0790, found 213.0785.

**Radical Cyclization of 12.** The procedure used for the preparation of **17** was followed. To a refluxing solution of the bromide **12** (*Z*/*E*, 2:1) (0.528 g, 1.50 mmol) and ACN (0.022 g, 0.09 mmol) in toluene (150 mL) was added a solution of *n*-$Bu_3SnH$ (0.481 g, 1.65 mmol), AIBN (0.015 g, 0.09 mmol), and ACN (0.015 g, 0.06 mmol) in toluene (2 mL) over 3 h via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 2 h with the concomitant addition of more AIBN (0.020 g). Evaporation of the solvent under reduced pressure gave an orange oil. The $^1H$ NMR of this mixture indicated the presence of **18a**, **18b**, **23**, and **32** in an approximate ratio of 2.8:1.2:1.0:2.5. The residue was dissolved in 10 mL of $Et_2O$ and treated with saturated KF solution (10 mL). After 30 min, the mixture was filtered through Celite, the layers were separated, and the aqueous solution was extracted with ethyl ether (4 × 40 mL). The combined organic solution was dried ($MgSO_4$) and concentrated. Flash chromatography (hexane–ethyl acetate, 4:1) of the residue gave first the reduction product **32** (0.067 g, 16%), then a 1:1 mixture of **18b** and **23** (0.145 g), and finally the more polar compound **18a** (0.130 g, 31%).

**Dimethyl 1-(2-propenyl)-1*H*-indole-2,3-dicarboxylate (32)**: colorless oil; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 8.14 (dt, 1 H, $J$ = 7.6, 1.3 Hz, Ar), 7.39–7.28 (m, 3 H, Ar), 5.95 (ddt, 1 H, $J$ = 17.0, 10.3, 5.2 Hz, C*H*=$CH_aH_b$), 5.20 (ddd, 1 H, $J$ = 10.3, 2.5, 1.4 Hz, CH=C$H_aH_b$), 5.04 (ddd, 1 H, $J$ = 17.0, 2.5, 1.7 Hz, CH=$CH_aH_b$), 4.88 (dt, 2 H, $J$ = 5.2, 1.7 Hz, $NCH_2$), 4.00 (s, 3 H, $OCH_3$), 3.94

(s, 3 H, $OCH_3$); IR ($CDCl_3$) 1726 (shoulder), 1705 $cm^{-1}$; EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.1006. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.99; H, 5.57; N, 5.06.

**Dimethyl 9,9a-Dihydro-3*H*-pyrrolo[1,2-*a*]indole-9,9a-dicarboxylate (18a).** The more polar, major isomer was obtained as a pale yellow solid. Recrystallization from ethanol gave pale yellow crystals, mp 79–80 °C: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.23–7.15 (m, 2 H, Ar), 6.90–6.84 (m, 2 H, Ar), 5.97 (ddd, 1 H, $J$ = 5.7, 2.0, 1.5 Hz, olefinic), 5.88 (ddd, 1 H, $J$ = 5.7, 2.6, 1.8 Hz, olefinic), 4.52 (s, 1 H, H-9), 4.35 (ddd, 1 H, $J$ = 15.7, 2.6, 1.4 Hz, H-3), 4.02 (dt, 1 H, $J$ = 15.7, 2.0 Hz, H-3'), 3.73 (s, 3 H, $OCH_3$), 3.65 (s, 3 H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 171.7 (C=O), 171.4 (C=O), 154.2 (s, Ar), 130.8 (C-1 or C-2), 130.7 (C-1 or C-2), 129.3 (d, Ar), 126.4 (s, Ar), 124.4 (d, Ar), 121.7 (d, Ar), 113.7 (d, Ar), 86.5 (C-9a), 61.7 (C-3), 55.0 (C-9), 52.4 ($OCH_3$), 52.3 ($OCH_3$); IR ($CDCl_3$) 1741 $cm^{-1}$; EIMS (20 eV) $m/z$ 273 (13), 214 (77), 182 (7), 154 (100); EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.0997. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.84; H, 5.53; N, 5.08.

The chromatographic fraction containing the mixture of **18b** and **23** was dissolved in $Et_2O$ and extracted with 6 M HCl following the procedure employed for the extraction of **13**. Evaporation of the $CH_2Cl_2$ solution containing the basic compounds yielded the minor isomer **18b** (0.0652 g, 16%) as an oil. Chromatographic purification (hexanes–ethyl acetate, 7:3) gave pure **18b** (0.051 g, 12%) as a pale yellow glass.

**Dimethyl 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indole-9,9a-dicarboxylate (18b)** (less polar, minor isomer): $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.26–7.18 (m, 2 H, Ar), 6.93 (td, 1 H, $J$ = 7.5, 1.0 Hz, Ar), 6.84 (d, 1 H, $J$ = 7.9 Hz), 6.06 (dt, 1 H, $J$ = 5.9, 1.8 Hz, olefinic), 5.90 (dt, 1 H, $J$ = 5.9, 2.3 Hz, olefinic), 4.77 (s, 1 H, H-9), 4.32 (ddd, 1 H, $J$ = 15.3, 2.6, 1.6 Hz, H-3), 4.02 (dt, 1 H, $J$ = 15.3, 2.1 Hz, H-3'), 3.80 (s, 3 H, $OCH_3$), 3.78 (s, 3 H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 173.0 (C=O), 170.6 (C=O), 153.6 (s, Ar), 131.2 (C-1 or C-2), 129.1 (d, Ar), 127.3 (C-1 or C-2), 126.5 (s, Ar), 125.7 (d, Ar), 121.6 (d, Ar), 113.1 (d, Ar), 85.7 (C-9a), 61.9 (C-3), 53.3 (C-9), 53.0 ($OCH_3$), 52.1 ($OCH_3$); IR ($CDCl_3$) 1739 $cm^{-1}$; EIMS (20 eV) $m/z$ 273 (16), 214 (72), 182 (8), 154 (100); EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.0996. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.79; H, 5.56; N, 5.07.

The ethereal extract containing the neutral products was washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography (hexane–ethyl acetate, 7:3) of the residue gave **23** (0.0393 g, 12%) as a glass.

**Radical Cyclization of 33.** To a refluxing solution of the iodide **33** (0.075 g, 0.263 mmol), *n*-$Bu_3SnH$ (0.0842 g, 0.289 mmol), and ACN (0.005 g, 0.02 mmol) in toluene (29 mL) was added a solution of AIBN (0.005 g, 0.03 mmol) in toluene (1 mL) over 2 h, via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 1 h. Evaporation of the solvent under reduced pressure furnished a yellow oil. TLC (hexane–ethyl acetate, 4:1) analysis of the crude material showed the presence of three main spots. The residue was dissolved in $Et_2O$ (30 mL) and extracted with 2 M HCl, following the procedure employed for the extraction of **13**. Evaporation of the $CH_2Cl_2$ solution containing the basic compounds yielded the tetrahydropyrroloindole **34** (0.021 g, 50%) as an oil. Chromatographic purification (hexanes–ethyl acetate, 9:1) afforded pure **34**[18a] (0.0189 g, 45%) as a colorless oil that darkened on standing.

**2,3,9,9a-Tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (34):** $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.15–7.06 (m, 2 H, Ar), 6.76 (td, 1 H, $J$ = 7.4, 1.0 Hz, Ar), 6.61 (d, 1 H, $J$ = 7.7 Hz), 3.94 (tdd, 1 H, $J$ = 9.2, 6.1, 2.9 Hz, H-9a), 3.44 (ddd, 1 H, $J$ = 10.7, 7.1, 5.2 Hz, H-3), 3.25–3.13 (m, 2 H, H-3', and H-9), 2.96 (dd, 1 H, $J$ = 16.0, 2.7 Hz, H-9'), 1.96–1.79 (m, 3 H, H-1, H-2, and H-2'), 1.41–1.27 (m, 1 H, H-1'); $^{13}C$ NMR ($CDCl_3$) $\delta$ 154.6 (s, Ar), 129.9 (s, Ar), 127.5 (d, Ar), 127.5 (d, Ar), 124.8 (d, Ar), 119.2 (d, Ar), 110.9 (d, Ar), 65.2 (C-9a), 52.2 (C-3), 33.9 (C-9), 31.3 (C-2), 25.8 (C-1); EIMS (20 eV) $m/z$ 160 (M + H, 7), 159 (M, 29), 158 (100), 130 (43); CIHRMS calcd for $C_{11}H_{14}N$ (M + H) 160.1126, found 160.1114. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.08; H, 8.13; N, 8.87.

The ethereal extract containing the neutral products was treated with KF solution and concentrated. Flash chromatography (hexane–ethyl acetate, 19:1) of the residue gave first 1-(1-propyl)-1*H*-indole (0.011 g, 26%)[19] and then the dihydropyrroloindole **35** (0.004 g, 10%).

**2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole (35)** was obtained as an off-white solid. Recrystallization from ethanol gave colorless crystals: mp 78–79 °C [lit.[18a] mp 79–80 °C (ethanol)]; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 7.57 (dd, 1 H, $J$ = 6.8, 1.4 Hz, Ar), 7.26 (m, 1 H, Ar), 7.17–7.05 (m, 2 H, Ar), 6.19 (d, 1 H, $J$ = 1.0 Hz, H-9), 4.08 (t, 2 H, $J$ = 7.0 Hz, H-3), 3.05 (t, 2 H, $J$ = 7.3 Hz, H-1), 2.63 (pent, 2 H, $J$ = 7.1 Hz, H-2); EIMS (20 eV) $m/z$ 157 (97), 156 (97), 130 (100), 129 (37), 84 (21); EIHRMS calcd for $C_{11}H_{11}N$ 157.0891, found 157.0904. Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.95; H, 7.01; N, 8.87.

**Acknowledgment.** This work was supported by a grant from the National Cancer Institute, NIH (CA-39976). We are grateful to Dr. Zhong-li Zheng for preliminary studies in this area. We thank Mr. Dan Pentek of the Yale Chemical Instrumentation Center for recording the high resolution mass spectra.

# The Use of $R_3SiSnR'_3$ in Organic Synthesis. A Novel Palladium-Catalyzed Tandem Transmetalation–Cyclization Reaction

Miwako Mori,* Naotake Kaneta, and Masakatsu Shibasaki*

*Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan*

*Received July 10, 1990 (Revised Manuscript Received October 22, 1990)*

The intramolecular coupling of vinyl triflates **12** with vinyl halides proceeded smoothly in the presence of $Bu_3SnSiMe_3$ (**1a**) and a palladium catalyst and gave cyclic products **13** via tandem intermolecular and intramolecular transmetalations.

## Introduction

Organometallic reagents that possess a metal–metal bond are synthetically useful. Among such reagents, those species that possess a Si–Sn bond are especially interesting because of the increasing use of organosilicon and organostannane compounds in organic synthesis. Recent reports have described the utility of $R_3SnSiR'_3$ (**1**).[1] For example, Mitchell[2] and Chenard[3] independently reported

(1) Schumann, H.; Ronecker, S. *Z. Naturforsch, Teil B* **1967**, *22*, 452.

0022-3263/91/1956-3486$02.50/0 