Studies in the Protection of Pyrrole and Indole Derivatives

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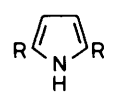
Treatment of pyrrole (**1a**), 2,5-dimethylpyrrole (**1b**), indole (**3a**), 2-methylindole (**3b**), 3-methylindole (**3c**), 2,3-dimethylindole (**3d**), 1,2,3,4-tetrahydro-9*H*-carbazole (**5a**), 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**), and 6,7,8,9,10,11-hexahydro-5*H*-cyclo-oct[*b*]indole (**5c**) with sodium hydride in tetrahydrofuran, followed by phenyl t-butyl carbonate (**8**) gives the corresponding *N*-t-butoxycarbonyl (t-BOC) derivatives [(**2a**), (**2b**), (**4a**), (**4b**), (**4c**), (**4d**), (**6a**), (**6b**), and (**6c**), respectively] in satisfactory yields. By using chlorodimethyl-t-butylsilane instead of (**8**), *N*-dimethyl-t-butylsilyl derivatives [(**10a**), (**10b**), (**11a**), (**11b**), (**11c**), (**11d**), (**12a**), and (**12b**)] are obtained, also in satisfactory yields. The use of the 2-(trimethylsilyl)ethoxycarbonyl (TEOC) group for the *N*-protection of the indole system, and the pivaloyloxymethyl (POM) group for the *N*-protection of the pyrrole and indole systems is also described.

The protection of the NH group of pyrrole[1] and indole[2] derivatives is of much importance in organic synthesis, and there are numerous reports in the literature of the use of specific protecting groups for this purpose. Alkyl (*e.g.*, benzyl,[3] triphenylmethyl,[4] and 2-phenylsulphonylethyl[1]), silyl (*e.g.*, dimethyl-t-butylsilyl[2,5] and tri-isopropylsilyl[6,7]), alkoxymethyl [*e.g.*, methoxymethyl,[8] benzyloxymethyl,[9] and 2-(trimethylsilyl)-ethoxymethyl[10]], acyl (*e.g.*, benzoyl,[11] phenylsulphonyl,[12] and t-butoxycarbonyl[13,14]), and other (*e.g.*, dimethylamino[15]) protecting groups have been used. In connection with some synthetic studies that we are at present undertaking in this laboratory, we required an *N*-protecting group for pyrrole and indole derivatives that could be: (i) readily introduced, (ii) removed under very mild conditions, and (iii) easily removed from the corresponding pyrroline or indoline system, obtained after the effective reduction of the 2,3-double bond.

We first investigated the preparation of t-butoxycarbonyl (t-BOC) derivatives of pyrrole and indole derivatives. Carpino and Barr originally reported[13] that the potassium salt of pyrrole reacted with t-butyl azidoformate (**7**) to give 1-(t-butoxycarbonyl)pyrrole (**2a**) in satisfactory yield. Hasan *et al.*[16] confirmed this result and showed that when indole was treated first with sodium hydride and then with t-butyl azidoformate (**7**) in tetrahydrofuran (THF) solution, 1-(t-butoxycarbonyl)-indole (**4a**) was obtained in high yield. Using essentially the same procedure,[14] we also converted 3-methylindole (**3c**) into its 1-(t-butoxycarbonyl) derivative (**4c**) in good yield; however, we found[14] that when the conjugate bases of 2-methylindole (**3b**), 2,3-dimethylindole (**3d**), 1,2,3,4-tetrahydro-9*H*-carbazole (**5a**) and 6,7,8,9,10,11-hexahydro-5H-cyclo-oct[*b*]indole (**5c**) were treated with t-butyl azidoformate (**7**) in THF, they were converted into the corresponding *N*-(t-butoxycarbonyl) derivatives [(**4b**), (**4d**), (**6a**), and (**6c**)] only in 11, 20, 46, and 19% yields, respectively. Significant quantities of other more complex products were obtained[14] in each of these reactions. We now report that when pyrrole (**1a**), 2,5-dimethylpyrrole (**1b**), indole (**3a**), 2-methylindole (**3b**), 3-methylindole (**3c**), 2,3-dimethylindole (**3d**), 1,2,3,4-tetrahydro-9*H*-carbazole (**5a**), 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) and 6,7,8,9,10,11-hexahydro-5*H*-cyclo-oct[*b*]indole (**5c**) are treated first with *ca.* 3 mol equiv. of sodium hydride and then with a slight excess of phenyl t-butyl carbonate (**8**) in THF at room temperature, no such complications arise and the corresponding *N*-(t-butoxycarbonyl) derivatives are all obtained in satisfactory yields [Table (entries nos. 1—9) and Experimental section]. After the completion of this part of the work, Grehn and Ragnarsson reported[17] that pyrrole, a number of substituted pyrroles, indole, and 3-methylindole (**3c**) react with di-t-butyl dicarbonate (**9**) in the presence of triethylamine and 4-dimethylaminopyridine in acetonitrile solution to give the corresponding t-BOC derivatives in good to high yields.

t-BOC Derivatives of pyrroles (Table, entries nos. 1 and 2) and indoles (entries nos. 3—9) not unexpectedly exhibited a singlet, integrating for 9 H and resonating at δ *ca.* 1.6 in their ^{1}H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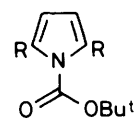
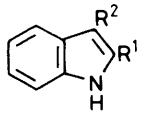
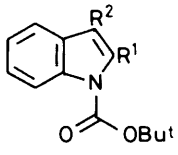
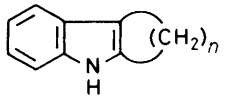
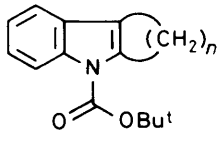
b; R = Me

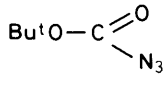

(2) a; R = H
b; R = Me

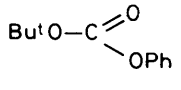

(3) a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = H, R^2 = Me$
d; $R^1 = R^2 = Me$


(4) a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = H, R^2 = Me$
d; $R^1 = R^2 = Me$


(5) a; $n = 4$
b; $n = 5$
c; $n = 6$


(6) a; $n = 4$
b; $n = 5$
c; $n = 6$


(7)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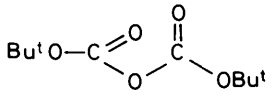
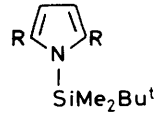

(9)

Table. Data relating to the protection of pyrrole and indole derivatives

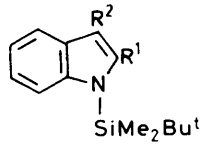
Entry no.	Substrate	Reagent	Product	M.p. (b.p.)[a]/°C	Yield (%)[b]	^{1}H N.m.r.[c]	^{13}C N.m.r.[c]
1	(**1a**)	(**8**)	(**2a**)	(98—99/19 mmHg)	80	1.59 (9 H, s)	27.98, 83.54, 148.99
2	(**1b**)	(**8**)	(**2b**)		67	1.59 (9 H, s)	27.97, 82.99, 150.41
3	(**3a**)	(**8**)	(**4a**)	(84/0.25 mmHg)	78	1.67 (9 H, s)	28.21, 83.66, 149.97
4	(**3b**)	(**8**)	(**4b**)	50—52	88	1.68 (9 H, s)	28.30, 83.59, 150.71
5	(**3c**)	(**8**)	(**4c**)		91	1.65 (9 H, s)	28.22, 83.14, 149.83
6	(**3d**)	(**8**)	(**4d**)	52	88	1.67 (9 H, s)	28.35, 83.23, 150.88
7	(**5a**)	(**8**)	(**6a**)	(126/0.25 mmHg)	84	1.65 (9 H, s)	28.32, 83.09, 150.72
8	(**5b**)	(**8**)	(**6b**)	57—58	71		28.30, 83.31, 150.91
9	(**5c**)	(**8**)	(**6c**)	59	74		28.35, 83.21, 150.62
10	(**1a**)	(**13**)	(**10a**)	(91/18 mmHg)	78	0.42 (6 H, s), 0.88 (9 H, s)	−5.51, 18.13, 25.87
11	(**1b**)	(**13**)	(**10b**)	(124/14 mmHg)	71	0.58 (6 H, s), 0.99 (9 H, s)	−0.12, 20.51, 26.81
12	(**3a**)	(**13**)	(**11a**)	41	79	0.60 (6 H, s), 0.93 (9 H, s)	−3.97, 19.49, 26.30
13	(**3b**)	(**13**)	(**11b**)		77	0.65 (6 H, s), 0.96 (9 H, s)	−0.48, 20.60, 26.81
14	(**3c**)	(**13**)	(**11c**)	72	68	0.57 (6 H, s), 0.92 (9 H, s)	−3.94, 19.49, 26.34
15	(**3d**)	(**13**)	(**11d**)	66—67	92	0.64 (6 H, s), 0.97 (9 H, s)	−0.29, 20.53, 26.83
16	(**5a**)	(**13**)	(**12a**)	54.5	74	0.65 (6 H, s), 0.98 (9 H, s)	−0.70, 20.46, 26.80
17	(**5b**)	(**13**)	(**12b**)	73—74	64	0.64 (6 H, s), 1.05 (9 H, s)	0.11, 19.90, 26.63
18	(**3b**)	(**14c**)	(**15**)	59	61	1.28 (2 H, m), 4.53 (2 H, m), 0.12 (9 H, s)	−1.58, 17.74, 65.39, 152.28
19	(**5b**)	(**14c**)	(**16**)	63	64	1.28 (2 H, m), 4.53 (2 H, m,), 0.13 (9 H, s)	−1.55, 17.80, 65.29, 152.50
20	(**1a**)	(**17**)	(**18**)	(66/14 mmHg)	78	1.16 (9 H, s), 5.79 (2 H, s)	26.88, 38.76, 70.95, 177.89
21	(**3a**)	(**17**)	(**19**)		65	1.13 (9 H, s), 6.08 (2 H, s)	26.87, 38.84, 68.61, 178.10
22	(**5b**)	(**17**)	(**20**)	64.5	73	1.15 (9 H, s), 6.08 (2 H, s)	26.95, 38.85, 66.30, 177.95

[a] B.p.s of liquid products are indicated in parentheses. In the cases where no melting or boiling point data are given, the products are liquids isolated by Kugelrohr distillation. [b] Yields of isolated products are given; these yields have not been optimized. [c] ^{1}H And ^{13}C n.m.r. spectra were measured in $CDCl_3$ solution at 250 and 62.9 MHz, respectively; only the signals relating to the resonance of the protons and carbon nuclei of the protecting groups are given.

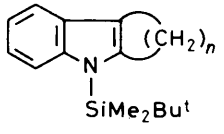
n.m.r. spectra. This signal may sometimes be obscured by other resonance signals (entries nos. 8 and 9). It is further apparent (Table and Experimental section) that the t-BOC derivatives (entries nos. 1—9) all exhibit three characteristic resonance signals at (i) *ca.* 28 (t-butyl methyl C), (ii) *ca.* 82 (quaternary t-butyl C) and (iii) *ca.* 150 p.p.m. (t-BOC carbonyl C) in their ^{13}C n.m.r. spectra. The t-BOC protecting group has been removed[16] from both pyrrole and indole derivatives by treatment with sodium methoxide in methanol–THF at room temperature, and from indole derivatives[16] by treatment with trifluoroacetic acid also at room temperature. We have found that this protecting group can conveniently be removed from indole derivatives by treatment with trifluoroacetic acid in dichloromethane solution at room temperature.



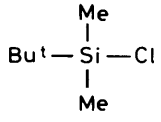
(**10**) a; R = H
b; R = Me



(**11**) a; $R^1 = R^2 = H$
b; R^1 = Me, R^2 = H
c; R^1 = H, R^2 = Me
d; $R^1 = R^2$ = Me



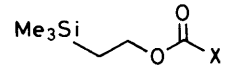
(**12**) a; *n* = 4
b; *n* = 5



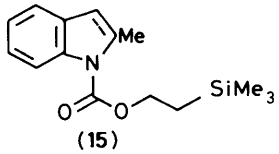
(**13**)

We next turned our attention to the preparation of dimethyl-t-butylsilyl derivatives. 1-(Dimethyl-t-butylsilyl)indole (**11a**) had previously been prepared[2] by treating indole first with n-butyl-lithium and then with chlorodimethyl-t-butylsilane (**13**) in THF, and the preparation of other 1-(trialkylsilyl)pyrroles,[18] including 1-(tri-isopropylsilyl)pyrrole,[6] had also been described. We now report that when pyrrole (**1a**), 2,5-dimethylpyrrole (**1b**), indole (**3a**), 2-methylindole (**3b**), 3-methylindole (**3c**), 2,3-dimethylindole (**3d**), 1,2,3,4-tetrahydro-9*H*-carbazole (**5a**) and 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) are treated first with sodium hydride in THF and then with a small excess of chlorodimethyl-t-butylsilane (**13**) at room temperature, the corresponding 1-(dimethyl-t-butylsilyl) derivatives [(**10a**), (**10b**), (**11a**), (**11b**), (**11c**), (**11d**), (**12a**), and (**12b**), respectively] are all obtained in satisfactory yields [Table (entries nos. 10—17) and Experimental section].

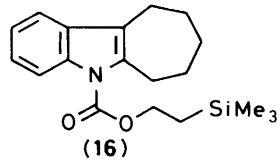
It can be seen (Table and Experimental section) that dimethyl-t-butylsilyl derivatives of pyrroles (Table, entries nos. 10 and 11) and indoles (entries nos. 12—17) exhibit two singlets, that integrate for 6 H and 9 H and resonate at *ca.* 0.6 and 1.0 p.p.m., respectively, in their ^{1}H n.m.r. spectra. It can further be seen that all of the latter derivatives (entries nos. 10—17) exhibit three characteristic resonance signals at (i) usually below zero (Si-methyl C), (ii) *ca.* 20 (quaternary t-butyl C) and (iii) *ca.* 26.5 (t-butyl methyl C) p.p.m. in their ^{13}C n.m.r. spectra. The dimethyl-t-butylsilyl group may rapidly be removed[6] by treating the pyrrole and indole derivatives with tetrabutylammonium fluoride in THF at room temperature.



(**14**) a; X = Cl
b; X = N_3
c; X = $OC_6H_4NO_2p$



(**15**)

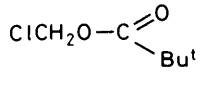


(**16**)

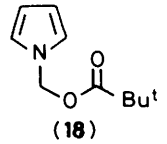
2-(Trimethylsilyl)ethoxycarbonyl (TEOC) has been suggested[19] as a protecting group for amino functions. The latter protecting group has been introduced[19] by allowing the amine to react either with 2-(trimethylsilyl)ethyl chloro- or azido-formate [(**14a**) or (**14b**)], and can be removed[19] either by treatment with fluoride ions (*e.g.* tetraethylammonium fluoride in acetonitrile solution) or, under acidic conditions (*e.g.* by treatment with trifluoroacetic acid). Thus the TEOC is potentially a very useful protecting group that can be removed either under the conditions required for the removal of a dimethyl-t-butylsilyl or a t-BOC group.

As 2-(trimethylsilyl)ethyl chloroformate (**14a**) has been reported[19] to decompose with time and the azidoformate (**14b**) would be expected[14] to be unsuitable for the present purposes, we have used 4-nitrophenyl 2-(trimethylsilyl)ethyl carbonate[20] (**14c**) to introduce the TEOC protecting group. The latter reagent (**14c**) was prepared by treating 2-(trimethylsilyl)ethanol with an approximately stoicheiometric quantity of 4-nitrophenyl chloroformate in the presence of quinoline in dichloromethane solution, and was isolated as a stable, low melting crystalline solid in 75% yield. When 2-methylindole (**3b**) and 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) are treated first with sodium hydride in THF and then with a small excess of 4-nitrophenyl 2-(trimethylsilyl)ethyl carbonate (**14c**) at room temperature, the corresponding *N*-[2-(trimethylsilyl)ethoxycarbonyl] derivatives [(**15**) and (**16**)] are obtained [Table (entries nos. 18 and 19) and Experimental section].

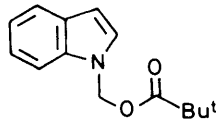
Both of the latter TEOC derivatives exhibit a singlet, integrating for 9 H, at δ *ca.* 0.1 and two multiplets, each integrating for 2 H, at δ *ca.* 1.3 and 4.5 in their ^{1}H n.m.r. spectra; these derivatives both exhibit four resonance signals at δ *ca.* −1.6 (Si-methyl C), *ca.* 17.8 (Si-methylene C), *ca.* 65.3 (O-methylene C), and *ca.* 152.4 (carbonyl C) in their ^{13}C n.m.r. spectra that can be assigned to the TEOC proecting group. The latter group was completely removed from compound (**16**) after it had been treated with *ca.* 2 mol equiv. of M-tetraethylammonium fluoride in acetonitrile solution[19] at room temperature for 1 h, and compound (**5b**) was isolated from the products in good yield.



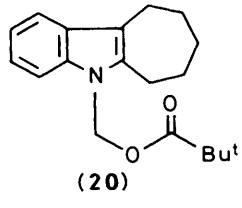
(**17**)



(**18**)



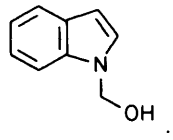
(**19**)



(**20**)

As indicated above, a number of alkoxymethyl groups [*e.g.* benzyloxymethyl[9] and 2-(trimethylsilyl)ethoxymethyl[10]] have been used for the *N*-protection of pyrrole and indole derivatives. In 1967, Rasmussen and Leonard reported[21] the use of an acyloxymethyl group, namely pivaloyloxymethyl (POM), for the *N*-protection of purine systems. It occurred to us that the POM group, which is stable both in mildly acidic and mildly basic media, would possibly be a useful *N*-protecting group in pyrrole and indole chemistry.* Furthermore, chloromethyl pivalate (**17**), which is required for the introduction of the POM protecting group, is a relatively inexpensive, commercially available reagent. We now report that when pyrrole (**1a**), indole (**3a**) and 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) are treated first with sodium hydride in THF and then with an excess of chloromethyl pivalate (**17**) at room temperature, the corresponding *N*-(pivaloyloxymethyl) derivatives [(**18**), (**19**), and (**20**), respectively] are obtained in satisfactory yields [Table (entries nos. 20—22) and Experimental section].

The POM derivatives [Table (entries nos. 20—22) and Experimental section] exhibit two singlets, integrating for 9 H and 2 H, at δ *ca.* 1.15 and *ca.* 6, respectively, in their ^{1}H n.m.r. spectra; these derivatives exhibit four characteristic resonance signals at δ *ca.* 27 (t-butyl methyl C), *ca.* 39 (quaternary t-butyl C), *ca.* 69 [above 69 for (**18**) and below 69 for (**19**) and (**20**); *N*-methylene C] and *ca.* 178 (carbonyl C) in their ^{13}C n.m.r. spectra. The unblocking of POM derivatives, like that of the corresponding alkoxymethyl derivatives,[8-10] is less straightforward than the unblocking of the other protected pyrrole and indole derivatives described above. Thus, when 1-(pivaloyloxymethyl)indole (**19**) is treated with methanolic sodium methoxide at room temperature, a mixture of indole and 1-(hydroxymethyl)indole (**21**) is obtained. However, when the



(**21**)

latter mixture is heated with very dilute potassium hydroxide (<0.3M)[10b] in THF–water (10:3 v/v) for 1 h, under reflux, the hydroxymethyl derivative (**21**) decomposes and indole may be isolated from the products in very high yield. It would therefore appear that the POM group is at least as convenient a protecting group for pyrrole and indole derivatives as any of the alkoxymethyl groups that have previously been used for this purpose.

Experimental

^{1}H and ^{13}C N.m.r. spectra were measured at 250 and 62.9 MHz, respectively, with a Bruker WM 250 spectrometer; tetramethylsilane was used as an internal standard. Merck silica gel H was used for short column chromatography.[22] Tetrahydrofuran (THF) was first dried over sodium and then heated, under reflux, with lithium aluminium hydride. Dichloromethane was dried by heating, under reflux, with phosphorus pentaoxide. The dried solvents were then distilled at atmospheric pressure. t-Phenylbutyl carbonate, 4-nitrophenyl chloroformate, 2-(trimethylsilyl)ethanol and chloromethyl pivalate were obtained from commercial sources.

Preparation of N-t-Butoxycarbonyl (t-BOC) *Pyrrole and Indole Derivatives.*—(a)*2,3-Dimethyl-1-(t-butoxycarbonyl)indole* (**4d**). 80% Sodium hydride dispersion in mineral oil (1.86 g, 62 mmol) was washed with light petroleum (b.p. 40—60 °C, 2 × 15 ml), and was then suspended in dry THF (25 ml) under an atmosphere of nitrogen at room temperature. A solution of 2,3-dimethylindole (3.02 g, 20.8 mmol) in THF (20 ml) was then added to the stirred reactants. After the ensuing effervescence had ceased, phenyl t-butyl carbonate (4.82 g, 24.8 mmol) was then added dropwise, and the reactants were stirred for a further period of 12 h at room temperature. Water (15 ml) was then added cautiously and the resulting mixture was extracted with ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$), evaporated under reduced pressure, and the oily residue was

* Dr. Theodora W. Greene (in 'Protective Groups in Organic Synthesis,' Wiley, New York, 1981, p. 271) refers to the preparation of *N*-(pivaloyloxymethyl)indole derivatives, but such derivatives are not described in Rasmussen and Leonard's paper.[21]

purified by short column chromatography on silica gel. The appropriate fractions, eluted with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1 v/v) were combined and evaporated under reduced pressure to give a colourless solid. Crystallization of this material from absolute ethanol gave 2,3-*dimethyl*-1-(*t-butoxycarbonyl*)*indole* (Found: C, 73.1; H, 7.75; N, 5.7. $C_{15}H_{19}NO_2$ requires C, 73.4; H, 7.8; N, 5.7%) as colourless needles (4.52 g, 88%), m.p. 52 °C; M^+, *m/z* 245; $\delta_H(CDCl_3)$ 1.67 (9 H, s), 2.18 (3 H, s), 2.52 (3 H, s), 7.22 (2 H, m), 7.41 (1 H, m), and 8.09 (1 H, m); $\delta_C(CDCl_3)$ 8.70, 13.88, 28.35, 83.23, 113.77, 115.31, 117.75, 122.30, 123.27, 130.81, 132.85, 135.67, and 150.88.

(b) 1-(*t-Butoxycarbonyl*)*pyrrole* (**2a**). Following the procedure described in (*a*) above, pyrrole (0.51 g, 7.6 mmol) was converted into 1-(*t-butoxycarbonyl*)*pyrrole*, b.p. 98—99 °C/19 mmHg (1.018 g, 80%); (Found: M^+, 167.0942. $C_9H_{13}NO_2$ requires 167.0946); $\delta_H(CDCl_3)$ 1.59 (9 H, s), 6.21 (2 H, m), and 7.24 (2 H, m); $\delta_C(CDCl_3)$ 27.98, 83.54, 111.86, 120.33, and 148.99.

(c) 2,5-*Dimethyl*-1-(*t-butoxycarbonyl*)*pyrrole* (**2b**). Following the procedure described in (*a*) above, 2,5-dimethylpyrrole (**1b**) (0.511 g, 5.4 mmol) was converted into 2,5-*dimethyl*-1-(*t-butoxycarbonyl*)*pyrrole* (0.71 g, 67%); [Found: $(M - 57)^+$, 138.0551. $C_7H_8NO_2$ requires 138.0555); $\delta_H(CDCl_3)$ 1.59 (9 H, s), 2.38 (6 H, s), and 5.78 (2 H, s); $\delta_C(CDCl_3)$ 16.37, 27.97, 82.99, 110.04, 131.05, and 150.41.

(d) 1-(*t-Butoxycarbonyl*)*indole* (**4a**). Following the procedure described in (*a*) above, indole (**3a**) (1.01 g, 8.6 mmol) was converted into 1-(*t-butoxycarbonyl*)*indole*, b.p. 84 °C/0.25 mmHg (1.465 g, 78%); (Found: M^+, 217.1095. $C_{13}H_{15}NO_2$ requires 217.1103); $\delta_H(CDCl_3)$ 1.67 (9 H, s), 6.56 (1 H, d, *J* 3.6 Hz), 7.2—7.35 (2 H, m), 7.55 (1 H, m), 7.59 (1 H, d, *J* 3.7 Hz), and 8.15 (1 H, m); $\delta_C(CDCl_3)$ 28.21, 83.66, 107.39, 115.30, 121.06, 122.77, 124.32, 126.01, 130.74, 135.37, and 149.97.

(e) 2-*Methyl*-1-(*t-Butoxycarbonyl*)*indole* (**4b**). Following the procedure described in (*a*) above, 2-methylindole (**3b**) (0.99 g, 7.6 mmol) was converted into 2-*methyl*-1-(*t-butoxycarbonyl*)*indole* (Found: C, 72.45; H, 7.4; N, 6.0. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%), m.p. 50—52 °C (from aqueous ethanol) (1.532 g, 88%); M^+, *m/z* 231; $\delta_H(CDCl_3)$ 1.68 (9 H, s), 2.59 (3 H, d, *J* 1.1 Hz), 6.31 (1 H, m), 7.20 (2 H, m), 7.43 (1 H, m), and 8.10 (1 H, m); $\delta_C(CDCl_3)$ 17.10, 28.30, 83.59, 107.97, 115.49, 119.49, 122.59, 123.10, 129.41, 136.55, 137.80, and 150.71.

(f) 3-*Methyl*-1-(*t-butoxycarbonyl*)*indole* (**4c**). Following the procedure described in (*a*) above, 3-methylindole (**3c**) (1.00 g, 7.6 mmol) was converted into 3-*methyl*-1-(*t-butoxycarbonyl*)*indole* (1.615 g, 91%) (Found: M^+, 231.1260. $C_{14}H_{17}NO_2$ requires 231.1259); $\delta_H(CDCl_3)$ 1.65 (9 H, s), 2.26 (3 H, d, *J* 1.3 Hz), 7.14—7.38 (3 H, m), 7.49 (1 H, m), and 8.11 (1 H, m); $\delta_C(CDCl_3)$ 9.59, 28.22, 83.14, 115.12, 116.32, 118.88, 122.27, 122.77, 124.19, 131.45, 134.46, and 149.83.

(g) 9-(*t-Butoxycarbonyl*)-1,2,3,4-*tetrahydro*-9H-*carbazole* (**6a**). Following the procedure described in (*a*) above, 1,2,3,4-tetrahydro-9*H*-carbazole (**5a**) (5.00 g, 29.2 mmol) was converted into 9-(*t-butoxycarbonyl*)-1,2,3,4-*tetrahydro*-9H-*carbazole*, b.p. 126 °C/0.25 mmHg (6.648 g, 84%) (Found: M^+, 271.1575. $C_{17}H_{21}NO_2$ requires 271.1572); $\delta_H(CDCl_3)$ 1.65 (9 H, s), 1.85 (4 H, m), 2.63 (2 H, m), 2.98 (2 H, m), 7.20 (2 H, m), 7.37 (1 H, m), and 8.12 (1 H, m); $\delta_C(CDCl_3)$ 21.12, 22.26, 23.69, 25.95, 28.32, 83.09, 115.38, 116.59, 117.42, 122.32, 123.31, 129.87, 135.63, 135.82, and 150.72.

(h) 5-(*t-Butoxycarbonyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (**6b**). Following the procedure described in (*a*) above, 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**)[23] (1.00 g, 5.4 mmol) was converted into 5-(*t-butoxycarbonyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (Found: C, 75.8; H, 8.1; N, 4.9. $C_{18}H_{23}NO_2$ requires C, 75.8; H, 8.1; N, 4.9%), m.p. 57—58 °C (from ethanol) (1.093 g, 71%); M^+, *m/z* 285; $\delta_H(CDCl_3)$ 1.4—1.95 (15 H, m), 2.75 (2 H, m), 3.23 (2 H, m), 7.22 (2 H, m), 7.41 (1 H, m), and 8.01 (1 H, m); $\delta_C(CDCl_3)$ 23.07, 26.27, 26.91, 28.10, 28.30, 30.33, 83.31, 115.08, 117.38, 121.29, 122.17, 123.04, 130.16, 135.39, 139.42, and 150.91.

(j) 5-(*t-Butoxycarbonyl*)-6,7,8,9,10,11-*hexahydro*-5H-*cyclooct*[b]*indole* (**6c**). Following the procedure described in (*a*) above, 6,7,8,9,10,11-hexahydro-5*H*-cyclo-oct[*b*]indole (**5c**)[24] (5.917 g, 29.7 mmol) was converted into 5-(*t-butoxycarbonyl*)-6,7,8,9,10,11-*hexahydro*-5H-*cyclo-oct*[b]*indole* (Found: C, 76.2; H, 8.7; N, 4.7. $C_{19}H_{25}NO_2$ requires C, 76.2; H, 8.4; N, 4.7%), m.p. 59 °C (from aqueous ethanol) (6.60 g, 74%); M^+, *m/z* 299; $\delta_H(CDCl_3)$ 1.1—1.8 (17 H, m), 2.68 (2 H, m), 3.09 (2 H, m), 7.0—7.4 (3 H, m), and 8.05 (1 H, m); $\delta_C(CDCl_3)$ 23.11, 24.61, 25.73, 26.73, 28.25, 29.40, 30.42, 83.21, 115.57, 117.39, 119.56, 122.24, 123.10, 129.57, 136.05, 136.76, and 150.62.

Preparation of Dimethyl-t-butylsilyl-pyrrole and -indole Derivatives.—(a) 1-(*Dimethyl-t-butylsilyl*)-2,3-*dimethylindole* (**11d**). 80% Sodium hydride dispersion in mineral oil (1.24 g, 41 mmol) was washed with light petroleum (b.p. 40—60 °C, 2 × 15 ml) and then suspended in dry THF (20 ml) under an atmosphere of nitrogen at room temperature. A solution of 2,3-dimethylindole (**3d**) (2.016 g, 13.9 mmol) in THF (15 ml) was then added to the stirred reactants. After the ensuing effervescence had ceased, a solution of chlorodimethyl-t-butylsilane (3.285 g, 21.8 mmol) in THF (15 ml) was added dropwise, and the reactants were stirred for a further period of 12 h at room temperature. Water (15 ml) was then added cautiously and the resulting mixture was extracted with ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$), evaporated under reduced pressure, and the dark oily residue was purified by short column chromatography. The appropriate fractions, eluted with light petroleum (b.p. 40—60 °C)–dichloromethane (7:3 v/v) were combined and evaporated under reduced pressure to give a pale yellow oil which solidified with time. Crystallization of this material from aqueous ethanol gave 1-(*dimethyl-t-butylsilyl*)-2,3-*dimethylindole* (Found: C, 74.3; H, 9.7; N, 5.3. $C_{16}H_{25}NSi$ requires C, 74.1; H, 9.7; N, 5.4%) as colourless needles, m.p. 66—67 °C (3.311 g, 92%); M^+, *m/z* 259; $\delta_H(CDCl_3)$ 0.64 (6 H, s), 0.97 (9 H, s), 2.21 (3 H, s), 2.40 (3 H, s), 7.07 (2 H, m), and 7.45 (2 H, m); $\delta_C(CDCl_3)$ −0.29, 8.94, 14.36, 20.53, 26.83, 111.27, 113.91, 117.58, 119.15, 120.36, 132.05, 137.15, and 141.49.

(b) 1-(*Dimethyl-t-butylsilyl*)*pyrrole* (**10a**). Following the procedure described in (*a*) above, pyrrole (**1a**) (0.50 g, 7.5 mmol) was converted into 1-(*dimethyl-t-butylsilyl*)*pyrrole*, b.p. 91 °C/18 mmHg (1.06 g, 78%) (Found: M^+, 181.1293. $C_{10}H_{19}NSi$ requires 181.1287); $\delta_H(CDCl_3)$ 0.42 (6 H, s), 0.88 (9 H, s), 6.32 (2 H, m), and 6.79 (2 H, m); $\delta_C(CDCl_3)$ −5.51, 18.13, 25.87, 110.36, and 123.79.

(c) 1-(*Dimethyl-t-butylsilyl*)-2,5-*dimethylpyrrole* (**10b**). Following the procedure described in (*a*) above, 2,5-dimethylpyrrole (0.504 g, 5.3 mmol) was converted into 1-(*dimethyl-t-butylsilyl*)-3,5-*dimethylpyrrole*, b.p. 124 °C/14 mmHg (0.79 g, 71%) (Found: M^+, 209.1602. $C_{12}H_{23}NSi$ requires 209.1600); $\delta_H(CDCl_3)$ 0.58 (6 H, s), 0.99 (9 H, s), 2.36 (6 H, s), and 5.89 (2 H, s); $\delta_C(CDCl_3)$ −0.12, 17.29, 20.51, 26.81, 110.61, and 130.69.

(d) 1-(*Dimethyl-t-butylsilyl*)*indole* (**11a**). Following the procedure described in (*a*) above, indole (**3a**) (0.506 g, 4.3 mmol) was converted into 1-(*dimethyl-t-butylsilyl*)*indole* (Found: C, 72.7; H, 9.2; N, 6.0. $C_{14}H_{21}NSi$ requires C, 72.7; H, 9.1; N, 6.05%), m.p. 41 °C (from aqueous ethanol) (0.794 g, 79%); M^+, *m/z* 231; $\delta_H(CDCl_3)$ 0.60 (6 H, s), 0.93 (9 H, s), 6.61 (1 H, m), 7.08—7.20 (3 H, m), 7.52 (1 H, m), and 7.63 (1 H, m); $\delta_C(CDCl_3)$ −3.97, 19.49, 26.30, 104.75, 113.84, 119.75, 120.61, 121.32, 130.94, 131.34, and 141.00.

(e) 1-(*Dimethyl-t-butylsilyl*)-2-*methylindole* (**11b**). Following the procedure described in (*a*) above, 2-methylindole (0.49 g, 3.7 mmol) was converted into 1-(*dimethyl-t-butylsilyl*)-2-*methyl*-

indole (0.711 g, 77%) (Found: M^+, 245.1598. $C_{15}H_{23}NSi$ requires 245.1600); $\delta_H(CDCl_3)$ 0.65 (6 H, s), 0.96 (9 H, s), 2.48 (3 H, d, *J* 0.8 Hz), 6.32 (1 H, m), 7.06 (2 H, m), and 7.48 (2 H, m); $\delta_C(CDCl_3)$ −0.48, 17.52, 20.60, 26.81, 106.17, 114.15, 119.17, 119.67, 120.29, 131.38, 142.00, and 142.72.

(f) 1-(*Dimethyl-t-butylsilyl*)-3-*methylindole* (**11c**). Following the procedure described in (*a*) above, 3-methylindole (**3c**) (0.532 g, 4.06 mmol) was converted into 1-(*dimethyl-t-butylsilyl*)-3-*methylindole* (Found: C, 73.4; H, 9.5; N, 5.7. $C_{15}H_{23}NSi$ requires C, 73.4; H, 9.45; N, 5.7%), m.p. 72 °C (from ethanol) 0.68 g, 68%; M^+, *m/z* 245; $\delta_H(CDCl_3)$ 0.57 (6 H, s), 0.92 (9 H, s), 2.31 (3 H, d, *J* 0.9 Hz), 6.93 (1 H, m), 7.13 (2 H, m), 7.46 (1 H, m), and 7.55 (1 H, m); $\delta_C(CDCl_3)$ −3.94, 9.65, 19.49, 26.34, 113.49, 113.76, 118.70, 119.16, 121.26, 128.22, 131.75, and 141.40.

(g) 9-(*Dimethyl-t-butylsilyl*)-1,2,3,4-*tetrahydro*-9H-*carbazole* (**12a**). Following the procedure described in (*a*) above, 1,2,3,4-tetrahydro-9*H*-carbazole (0.519 g, 2.8 mmol) was converted into 9-(*dimethyl-t-butylsilyl*)-1,2,3,4-*tetrahydro*-9H-*carbazole* (Found: C, 75.9; H, 9.6; N, 4.9. $C_{18}H_{27}NSi$ requires C, 75.7; H, 9.5; N, 4.9%), m.p. 54.5 °C (from ethanol) (0.642 g, 74%); M^+, *m/z* 285; $\delta_H(CDCl_3)$ 0.65 (6 H, s), 0.98 (9 H, s), 1.89 (4 H, m), 2.78 (4 H, m), 7.09 (2 H, m), 7.45 (1 H, m), and 7.51 (1 H, m); $\delta_C(CDCl_3)$ −0.70, 20.46, 21.46, 22.75, 24.22, 26.80, 113.64, 113.99, 117.26, 119.21, 120.56, 130.88, 140.20, and 141.61.

(h) 5-(*Dimethyl-t-butylsilyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (**12b**). Following the procedure described in (*a*) above, 5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (**5b**) (0.996 g, 5.4 mmol) was converted into 5-(*dimethyl-t-butylsilyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (Found: C, 76.3; H, 9.8; N, 4.75. $C_{19}H_{29}NSi$ requires C, 76.2; H, 9.8; N, 4.7%), m.p. 73—74 °C (from ethanol) (1.03 g, 64%); M^+, *m/z* 299; $\delta_H(CDCl_3)$ 0.64 (6 H, s), 1.05 (9 H, s), 1.74 (4 H, m), 1.92 (2 H, m), 2.82 (2 H, m), 2.95 (2 H, m), 7.08 (2 H, m), and 7.47 (2 H, m); $\delta_C(CDCl_3)$ 0.11, 19.90, 24.11, 26.63, 27.26, 27.65, 30.29, 32.04, 114.06, 117.10, 118.12, 119.11, 119.99, 131.78, 140.74, and 144.53.

4-*Nitrophenyl* 2-(*Trimethylsilyl*)*ethyl Carbonate*[20] (**14c**).—2-(Trimethylsilyl)ethanol (5.9 g, 49.9 mmol) and redistilled quinoline (7.2 g, 55.7 mmol) were dissolved in dry dichloromethane (40 ml). A solution of 4-nitrophenyl chloroformate (10.13 g, 50.3 mmol) in dichloromethane (20 ml) was added dropwise to the stirred, cooled (water bath) solution in such a way that the temperature did not rise above 30 °C, and the reaction was then allowed to proceed at room temperature. After 12 h, water (50 ml) was added, the layers were separated, and the aqueous layer was back extracted with dichloromethane (2 × 20 ml). The organic layers were combined, washed with water (2 × 50 ml) and 6M-hydrochloric acid, dried ($MgSO_4$), and evaporated under reduced pressure. Crystallization of the solid residue obtained from absolute ethanol gave 4-*nitrophenyl* 2-(*trimethylsilyl*)*ethyl carbonate* (Found: C, 50.7; H, 6.0; N, 4.9. $C_{12}H_{17}NO_5$ Si requires C, 50.9; H, 6.05; N, 4.9%) as colourless needles (10.55 g, 75%), m.p. 35 °C; $\delta_H(CDCl_3)$ 0.09 (9 H, s), 1.16 (2 H, m), 4.39 (2 H, m), 7.38 (2 H, m), and 8.28 (2 H, m); $\delta_C(CDCl_3)$ −1.55, 17.56, 68.24, 121.84, 125.28, 145.37, 152.51, and 155.72.

Preparation of N-[2-(*Trimethylsilyl*)*ethoxycarbonyl*]*indole Derivatives*.—(a) 2-*Methyl*-1-[2-(*trimethylsilyl*)*ethoxycarbonyl*]*indole* (**15**). 80% Sodium hydride dispersion in mineral oil (0.07 g, 2.4 mmol) was washed with light petroleum (b.p. 40—60 °C, 2 × 2 ml), and was then suspended in dry THF (5 ml) under an atmosphere of nitrogen at 0 °C (ice bath). A solution of 2-methylindole (**3b**) (0.10 g, 0.76 mmol) in THF (2 ml) was then added to the stirred reactants. After the ensuing effervescence had ceased, a solution of 4-nitrophenyl 2-(trimethylsilyl)ethyl carbonate (0.31 g, 1.1 mmol) in THF (3 ml) was added dropwise and the reactants were allowed to warm up to room temperature. After 2 h, water (5 ml) was added cautiously and the resulting mixture was extracted with ether (2 × 25 ml). The combined extracts were dried ($MgSO_4$), evaporated under reduced pressure, and the residue was purified by short column chromatography on silica gel. The appropriate fractions, eluted with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1 v/v) were combined and evaporated under reduced pressure. Crystallization of the residue from aqueous ethanol gave 2-*methyl*-1-[2-(*trimethylsilyl*)*ethoxycarbonyl*]*indole* (Found: C, 65.05; H, 7.6; N, 5.0. $C_{15}H_{21}NO_2Si$ requires C, 65.4; H, 7.7; N, 5.1%) as colourless crystals, m.p.59 °C (0.128 g, 61%); M^+, *m/z* 275; $\delta_H(CDCl_3)$ 0.12 (9 H, s), 1.28 (2 H, m), 2.63 (3 H, d, *J* 1.1 Hz), 4.53 (2 H, m), 6.35 (1 H, m), 7.23 (2 H, m), 7.45 (1 H, m), and 8.14 (1 H, m); $\delta_C(CDCl_3)$ −1.58, 16.84, 17.74, 65.39, 108.24, 115.56, 119.50, 122.74, 123.17, 129.47, 136.37, 137.80, and 152.28.

(b) 5-[2-(*Trimethylsilyl*)*ethoxycarbonyl*]-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (**16**). Following the procedure described in (*a*) above, 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) (0.10 g, 0.54 mmol) was converted into 5-[2-(*trimethylsilyl*)-*ethoxycarbonyl*]-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole*, m.p. 63 °C (0.115 g, 64%) [Found: M^+, 329.1815. $C_{19}H_{27}NO_2Si$ requires 329.1811]; $\delta_H(CDCl_3)$ 0.13 (9 H, s), 1.28 (2 H, m), 1.85 (6 H, m), 2.78 (2 H, m), 3.31 (2 H, m), 4.53 (2 H, m), 7.24 (2 H, m), 7.44 (1 H, m), and 8.08 (1 H, m); $\delta_C(CDCl_3)$ −1.55, 17.80, 23.07, 26.25, 26.85, 27.87, 30.31, 65.29, 115.34, 117.40, 121.62, 122.37, 123.15, 130.31, 135.29, 139.45, and 152.50.

Preparation of N-*Pivaloyloxymethyl* (POM) *Pyrrole and Indole Derivatives*.—(a) 1-(*Pivaloyloxymethyl*)*indole* (**19**). 80% Sodium hydride dispersion in mineral oil (0.079 g, 2.6 mmol) was washed with light petroleum (b.p. 40—60 °C, 2 × 2 ml), and was then suspended in dry THF (10 ml) under an atmosphere of nitrogen at room temperature. A solution of indole (**3a**) (0.10 g, 0.85 mmol) in THF (2 ml) was then added to the stirred reactants. After the ensuing effervescence had ceased, a solution of chloromethyl pivalate (0.276 g, 1.83 mmol) in THF (1 ml) was added. After 5 min, the products were poured into 2M-potassium phosphate buffer (pH 4, 5 ml) and the resulting mixture was extracted with ether. The combined ether extracts were dried ($MgSO_4$), evaporated under reduced pressure, and the residue was distilled in a Kugelrohr apparatus (oven temperature, 150 °C, 18 mmHg) to give 1-(*pivaloyloxymethyl*)-*indole* (0.128 g, 65%) (Found: M^+, 231.1259. $C_{14}H_{17}NO_2$ requires 231.1259); $\delta_H(CDCl_3)$ 1.13 (9 H, s), 6.08 (2 H, s), 6.52 (1 H, m), 7.1—7.3 (3 H, m), 7.49 (1 H, m), and 7.61 (1 H, m); $\delta_C(CDCl_3)$ 26.87, 38.84, 68.61, 103.40, 109.53, 120.56, 120.96, 122.39, 128.52, 129.03, 136.18, and 178.10.

(b) 1-(*Pivaloyloxymethyl*)*pyrrole* (**18**). Following the procedure described in (*a*) above, pyrrole (0.50 g, 7.45 mmol) was converted in 1-(*pivaloyloxymethyl*)*pyrrole*, b.p. 66 °C/14 mmHg (1.05 g, 78%) (Found: M^+, 181.1097. $C_{10}H_{15}NO_2$ requires 181.1103); $\delta_H(CDCl_3)$ 1.16 (9 H, s), 5.79 (2 H, s), 6.18 (2 H, m), and 6.83 (2 H, m); $\delta_C(CDCl_3)$ 26.88, 38.76, 70.95, 109.68, 121.72, and 177.89.

(c) 5-(*Pivaloyloxymethyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (**20**). Following the procedure described in (*a*) above, 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (0.095 g, 0.51 mmol) was converted into 5-(*pivaloyloxymethyl*)-5,6,7,8,9,10-*hexahydrocyclohept*[b]*indole* (Found: C, 76.1; H, 8.5; N, 4.8. $C_{19}H_{25}NO_2$ requires C, 76.2; H, 8.4; N, 4.7%) as colourless needles, m.p. 64.5 °C (0.112 g, 73%); M^+, *m/z* 299, $\delta_H(CDCl_3)$ 1.15 (9 H, s), 1.7—2.0 (6 H, m), 2.81 (2 H, m), 2.89 (2 H, m), 6.08 (2 H, s), 7.15 (2 H, m), and 7.44 (2 H, m); $\delta_C(CDCl_3)$ 24.20, 25.95, 26.95, 28.06, 31.52, 38.85, 66.30, 109.18, 115.95, 117.64, 120.01, 121.33, 128.68, 135.84, 138.36, and 177.95.

Removal of the t-Butoxycarbonyl (t-BOC) *Protecting Group from* 5-(*t-Butoxycarbonyl*)-5,6,7,8,9,10- *hexahydrocyclohept-*

[b]*indole* (**6b**).—Trifluoroacetic acid (0.20 ml, 0.30 g, 2.6 mmol) was added to a stirred solution of the substrate (**6b**) (0.10 g, 0.35 mmol) in dichloromethane (1.0 ml) at room temperature. After 5 h, the products were poured into saturated aqueous sodium hydrogen carbonate (15 ml). The resulting mixture was extracted with dichloromethane (2 × 5 ml), and the extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure to give 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5b**) as a colourless solid (0.062 g, 96%). After recrystallization from methanol, the product had m.p. 144.5 °C (lit.,[23] 144 °C).

Removal of the Dimethyl-t-butylsilyl Protecting Group from 1-(Dimethyl-t-butylsilyl)pyrrole (**10a**).—A 1M-solution of tetrabutylammonium fluoride in THF (1.83 ml, 1.83 mmol) was added to a stirred solution of 1-(dimethyl-t-butylsilyl)pyrrole (0.299 g, 1.65 mmol) in dry THF (2.0 ml) at room temperature. After 1 min, the products were poured into saturated aqueous sodium hydrogen carbonate (25 ml) and the resulting mixture was extracted with dichloromethane (2 × 15 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure, below room temperature. The residue was chromatographed on silica gel with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1 v/v) as the eluting solvent. Careful evaporation of the appropriate fractions gave pyrrole (**1a**) (0.104 g, 94%) as a colourless oil. The product obtained was identical (^1H n.m.r., t.l.c.) with authentic material.

Removal of the 2-(Trimethylsilyl)ethoxycarbonyl Protecting Group from 5-[2-(Trimethylsilyl)ethoxycarbonyl]-5,6,7,8,9,10-hexahydrocyclohept[b]*indole* (**16**).—A 1M-solution of tetraethylammonium fluoride in acetonitrile (1.0 ml, 1.0 mmol) was added to a stirred solution of 5-[2-(trimethylsilyl)ethoxycarbonyl]-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (0.17 g, 0.52 mmol) in acetonitrile (1 ml) at room temperature. After 1 h, the products were poured into saturated aqueous sodium hydrogen carbonate (25 ml), and the resulting mixture was extracted with dichloromethane (2 × 15 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a colourless solid. Recrystallization of this material from methanol gave 5,6,7,8,9,10-hexahydrocyclohept-[*b*]indole (**5b**) as colourless crystals (0.082 g, 86%), m.p. 144 °C. The product obtained was identical (^1H n.m.r., t.l.c.) with authentic (**5b**).

Reaction Between 1-(Pivaloyloxymethyl)indole (**19**) *and Sodium Methoxide in Methanol.*—A 4.4M-solution of sodium methoxide in methanol (0.15 ml, 0.66 mmol) was added to a stirred solution of 1-(pivaloyloxymethyl)indole (0.105 g, 0.45 mmol) in dry methanol (2 ml) at room temperature. After 40 min, the products were evaporated under reduced pressure and the residue dissolved in water (10 ml). The solution was extracted with dichloromethane (2 × 10 ml), and the combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residual oil was fractionated by short column chromatography on silica gel with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1 v/v) as the eluting solvent. Evaporation of the appropriate fractions gave (i) indole (**3a**) [0.027 g, 50%), identical (^1H n.m.r., t.l.c.) to authentic material] and (ii) 1-(hydroxymethyl)indole (0.02 g, 30%). The latter compound was characterized by mass spectrometry [Found: M^+, 147.0675. C_9H_9NO requires 147.0684]; $\delta_H(CDCl_3)$ 2.73 (1 H, br s), 5.49 (2 H, s), 6.51 (1 H, d, *J* 3.0 Hz), 7.1—7.3 (3 H, m), 7.40 (1 H, m), and 7.62 (1 H, m); $\delta_C(CDCl_3)$ 69.79, 102.99, 109.47, 120.38, 121.16, 122.25, 127.29, 129.30, and 135.68).

Removal of the Pivaloyloxymethyl (*POM*) *Protecting Group from* (*Pivaloyloxymethyl*)*indole* (**19**).—4.4M-Methanolic sodium methoxide (0.30 ml, 1.3 mmol) was added to a stirred solution of 1-(pivaloyloxymethyl)indole (0.204 g, 0.89 mmol) in dry methanol (4 ml) at room temperature. After 20 min, the reaction solution was poured into water (20 ml) and the products were extracted with ether (25 ml). The ethereal layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in THF (20 ml) and aqueous potassium hydroxide (0.12M; 6ml, 0.72 mmol) was added. The resulting mixture was heated, under reflux, for 1 h and the products were poured into water (20 ml). The mixture obtained was extracted with ether (2 × 10 ml), and the dried ($MgSO_4$) combined extracts were evaporated to give indole (0.098 g, 95%; identified by t.l.c., ^1H n.m.r.) as a crystalline solid.

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