Convenient Procedure for the Synthesis of 2-Monoalkylated Indol-3-ones

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2-Alkyl-1,2-dihydroindol-3-ones are prepared from readily available 1-acetyl-2-methoxy-1,2-dihydroindol-3-one by alkylation, reduction with sodium borohydride, and demethoxylation of the resulting 3-hydroxy-2-methoxy-2,3-dihydroindoles with Lewis acids. The stereochemistry of the reduction is also described.

1,2-Dihydroindol-3-ones are useful synthetic intermediates for the synthesis of biologically active compounds such as indomethacin,[1] serotonin,[2] and ellipticine.[3] Although several methods for the synthesis of 1,2-dihydroindol-3-ones are known,[4–6] 2-monosubstituted 1,2-dihydroindol-3-ones are more difficult to obtain than are the corresponding 2-unsubstituted derivatives. Therefore the introduction of a substituent into the 2-position of the indolinones would seem to be a convenient method. However, monoalkylation of the 2-unsubstituted indolinone and its *O*-acetate with methyl iodide,[7] allyl bromide,[8] and acrylonitrile[9] is difficult and gives not the expected 2-monoalkylate but the corresponding 2,2-disubstituted indolinone. Recently, the condensation of 1,2-dihydroindol-3-ones with benzaldehydes followed by catalytic reduction to afford 2-benzyl derivatives was reported.[10] Continuing our study on the chemistry of 1,2-dihydroindol-3-ones,[11–14] we now report the convenient synthesis of 2-monoalkylated 1,2-dihydroindol-3-ones **5** from readily available 1-acetyl-2-methoxy-1,2-dihydroindol-3-one[15] **1** by alkylation, reduction, and demethoxylation, and we also describe the stereochemistry of the reduction of 2-methoxy-1,2-dihydroindol-3-ones **1** and **2**.

Results and Discussion

Alkylation of 1-acetyl-2-methoxy-1,2-dihydroindol-3-one **1** with alkyl halides under two-phase-transfer catalytic reaction conditions[16] (procedure A) at room temperature gave 2-alkyl-2-methoxyindolinones **2a–d** in good yield (Table 1). Since, in the case of methylation, procedure A gave exceptionally low yields, the reaction of the indolinone **1** with methyl iodide in the presence of sodium hydride (procedure B) was carried out to afford the 2-methylindolinone **2e** in 53% yield. The alkylated product **2f** was obtained by the Michael addition of the indolinone **1** to acrylonitrile in the presence of triethylamine (procedure C). Those structures were assigned on the basis of spectral data; the isomeric structure **3** was readily ruled out by the appearance of the IR absorption due to the 3-keto group in the 1732–1725 cm^{-1} region.

Reduction of the 2-alkylindolinones **2** and **1** with sodium borohydride gave *trans*- and/or *cis*-3-hydroxy-2-methoxy-2,3-dihydroindoles **4** in high yield (Table 2). The structures were established from spectral evidence, and the stereochemical assignments to the *trans*/*cis*-isomers of the indoles **4** were elucidated by their NOE measurements (Tables 3 and 4). The signal for the proton at the 3-position of the *trans*-isomer of compounds **4** appeared in the range δ 5.3–5.5, probably owing to the anisotropic effect of the methoxy group, to lower field than that (δ 5.1–4.9) of the *cis*-isomer of compounds **4**. The ratios of *trans*-:*cis*-isomers of the indoles **4b** and **4c** were determined by means of ^1H NMR spectroscopy (Table 2).

The stereochemistry of the reduction was sensitive to the bulk of the substituent R at the 2-position; the indoline **2** containing a smaller substituent gave predominantly the *cis*-indole **4** (Table 2). The steric course of the reduction is determined by a combination of steric interference and electrostatic effects in the transition state.[17] In the case of the indolinone **2** with a small substituent, the incoming hydride ion prefers to be antiperiplanar to the methoxy group on account of the polar–polar repulsion with the methoxy group rather than the minor steric repulsion with the substituent R (transition state **A**). On the other hand, the reduction of an indolinone **2** bearing a bulky substituent may be governed by steric interference to give preferentially the *trans*-indole **4**.

The sodium borohydride reduction of the 2-methoxyindolinones **1** and **2** proceeds more rapidly (0.5–1 h) than does that of 2-methyl-2-phenyl-1,2-dihydroindol-3-one[18] and the corresponding indan-1-one[19] (10–20 h) under similar conditions. This can be explained in terms of the activation of the carbonyl reactivity of substrates **1** and **2** owing to the inductive effect of the methoxy group and the ring nitrogen atom.

When the 2,3-dihydroindoles **4a** and **4f** were allowed to react with tin(IV) chloride at 0 °C, demethoxylation occurred smoothly to give the 1,2-dihydroindole-3-ones **5a** and **5f** in 64 and 93% yield, respectively. Similar treatment of the indole **4b**, however, gave not the expected indolinone **5b** but instead the

Table 1 Alkylation of 1-acetyl-2-methoxy-1,2-dihydroindol-3-one **1**

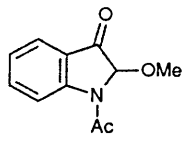
Product	Procedure[a]	Yield (%)[b]	$\nu_{max}(CHCl_3)/cm^{-1}$
2a	A	72	1732, 1675
2b	A	96	1732, 1674
2c	A	76	1730, 1675
2d	A	55	1729, 1675
2e	A	7	1725, 1675
	B	53	
2f	C	39	2256, 1731, 1684

[a] A; RX, 33% NaOH, TEBA (cat.), benzene, room temperature; B; MeI, NaH, dimethylformamide room temperature; C; acrylonitrile, triethylamine, Bu^{t}OH, reflux. [b] Isolated yields.

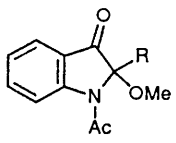
Table 2 Reduction of the indol-3-ones **1**, **2a–c** and **2f**

Reactant	Product	R	Yield (%)[a]	Ratio of **4**[b] *trans*:*cis*
2a	**4a**	CH_2Ph	99	100:0
2b	**4b**	$CH_2CH{=}CMe_2$	96	38:62
2c	**4c**	$CH_2CH{=}CH_2$	90	24:76
2f	**4f**	CH_2CH_2CN	96	0:100
1	**4g**	H	90	0:100

[a] Isolated yield. [b] The ratio was determined by ^1H NMR spectroscopic analysis of the reaction mixture.

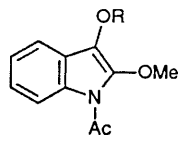


1



2

a; R = CH_2Ph
b; R = $CH_2CH{=}CMe_2$
c; R = $CH_2CH{=}CH_2$
d; R = $CHMe(4\text{-}C_5H_4N)$
e; R = Me
f; R = CH_2CH_2CN



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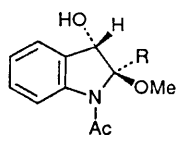
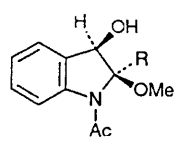
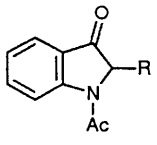


trans-4



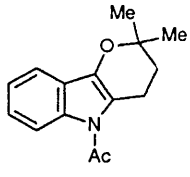
cis-4

a; R = CH_2Ph
b; R = $CH_2CH{=}CMe_2$
c; R = $CH_2CH{=}CH_2$
f; R = CH_2CH_2CN
g; R = H



5

a; R = CH_2Ph
b; R = $CH_2CH{=}CMe_2$
c; R = $CH_2CH{=}CH_2$
f; R = CH_2CH_2CN



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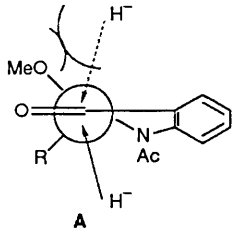
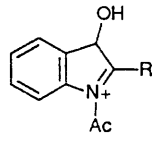


A



B

Table 3 ^1H NMR spectral data [400 MHz; $\delta(CD_3CN)$] of 2-methoxy-2,3-dihydroindol-3-ols **4a–c** and **4f***

Compound	3-H	CH_2	OH	COMe	OMe	Aromatic	Others
trans-**4a**	5.46(s)	3.19(d[i]) 3.45(br s)	4.15(s)	2.00(s)	3.33(s)	7.01 (1 H, t[e]), 7.05–7.2 (6 H, m), 7.27 (1 H, d[e]), 7.92 (1 H, br s)	
trans-**4b**	5.33(br s)	2.71(dd[f,j]) 2.97(br s)	3.18(d[e])	2.33(s)	3.20(s)	7.08 (1 H, t[e]), 7.25 (1 H, t[e]), 7.33 (1 H, d[e]), 8.08 (1 H, br s)	1.50 (3 H, s, Me), 1.56 (3 H, s, Me), 4.96 (1 H, t[e], =CH)
cis-**4b**	4.94(s)	2.75–2.90(m)	3.95(br)	2.37(s)	3.18(s)	7.09 (1 H, t[e]), 7.26 (1 H, t[e]), 7.32 (1 H, d[e]), 8.11 (1 H, br s)	1.63 (3 H, s, Me), 1.65 (3 H, s, Me), 4.97 (1 H, t[e], =CH)
trans-**4c**	5.44(s)	2.75(dd[f,i]) 3.15(br s)	4.05(d[d])	2.36(s)	3.20(s)	7.08 (1 H, t[f]), 7.25 (1 H, t[f]), 7.34 (1 H, d[f]), 8.09 (1 H, br s)	4.87 (1 H, d[g], =CH), 5.05 (1 H, d[l], =CH), 5.36 (1 H, br, =CH)
cis-**4c**	5.09(d[c])	2.86(dd[e,i]) 2.94(dd[d,i])	3.91(d[c])	2.39(s)	3.19(s)	7.09 (1 H, t[f]), 7.26 (1 H, t[f]), 7.32 (1 H, d[f]), 8.09 (1 H, br s)	5.10 (1 H, dd[b,g], =CH), 5.21 (1 H, dd[b,k], =CH), 5.66 (1 H, ddt[e,g,k], =CH)
cis-**4f**	5.06(d[e])	2.34(ddd[e,f,h]) 2.52(ddd[a,f,h])	3.97(s)	2.39(s)	3.20(s)	7.12 (1 H, t[e]), 7.29 (1 H, t[e]), 7.35 (1 H, d[e]), 7.98 (1 H, br s)	2.54 (1 H, ddd[a,f,h] CHCN) 2.68 (1 H, br m, CHCN)

* Coupling constants (J); [a] 1.5 Hz, [b] 2 Hz, [c] 5 Hz, [d] 6 Hz, [e] 7 Hz, [f] 8 Hz, [g] 10 Hz, [h] 12 Hz, [i] 14 Hz, [j] 16 Hz, [k] 17 Hz, [l] 18 Hz.

Table 4 NOE difference spectral data for the 2,3-dihydroindoles **4a–c** and **4f**

		Irradiation (↓) and enhancement (%)		
Compound	Geometry	3-H	CH_2	OH
4a	*trans*	↓	none	
			↓	2.4
4b	*trans*	↓	none	
	cis	4.3	↓	
4c	*trans*	none	↓	
	cis	2.8	↓	
4f	*cis*	↓	5.0	

pyrano[3,2-*b*]indole **6** in 16% yield, whose structure was confirmed by its elemental and spectral data. Therefore, by use of trimethylsilyl (TMS) triflate instead of tin(IV) chloride, the desired indolinone **5b** was obtained in 81% yield along with the pyranoindole **6** in low yield (4%). Since TMS triflate is a powerful silylating and oxophilic agent,[20] the initial silylation of the 3-hydroxy group in the indole **4b** may prevent acyclization of substrate **4b** to the tricycle **6**. Similarly the reaction of the indole **4c** with TMS triflate gave the indolinone **5c** in 77% yield. On storage in deuteriochloroform at room temperature for a week, the *cis*-indole **4b** was nearly quantitatively converted into the indolinone **5b**, but the *trans*-isomer remained unchanged (checked by TLC and ^1H NMR). This may indicate that the thermal decomposition affected by the stereochemistry of the indole **4b** arises from *anti*-elimination of methanol; in contrast, the Lewis acid-accelerated demethoxylation, irrespective of the stereochemistry, proceeds *via* an indoleninium intermediate (B).

Experimental

All m.p.s are uncorrected, and were measured on a Yanagimoto micromelting point apparatus. B.p.s were determined with a Buchi GKP-50 apparatus. IR spectra were recorded with a Hitachi 270–30 spectrophotometer. ^1H NMR spectra were determined with JEOL JNM-PMX 60 and GX-400 spectrometers with tetramethylsilane as internal standard. J Values are given in Hz. Mass spectra were obtained with a JEOL JMS-

DX302 instrument with a direct-inlet system operating at 70 eV. Elemental analyses were obtained by using a Perkin-Elmer Model 240B elemental analyser. Column chromatography was carried out on silica gel (Kanto Chemical Co. Inc., 100–200 mesh). Preparative TLC (PLC) was carried out on Merk silica gel 60 PF-254. 1-Acetyl-2-methoxy-1,2-dihydroindol-3-one[15] **1** and 1-(4-pyridyl)ethyl bromide hydrobromide[21] were prepared according to the reported procedure.

General Procedure for the Alkylation of the Indolinone **1**.—*Procedure A*. To a solution of the indolinone **1** (1 mmol), alkyl halide (5 mmol), and triethylbenzylammonium bromide (TEBA, 2–5 mg) in benzene (10 cm^3) was added 33% aq. NaOH (5 cm^3), and the mixture was vigorously stirred at room temperature for a designated period (4–6 h) under argon. The reaction mixture was extracted with benzene (100 cm^3), and the extract was washed with water and dried over $MgSO_4$. Work-up of the extract gave a residue, which was chromatographed on a silica gel column with $CHCl_3$ or CH_2Cl_2–ethyl acetate (2:1, for **2d**) as eluent to give the corresponding 2-alkyl-1,2-dihydroindol-3-one **2**. The IR spectral data of products **2a–f** are shown in Table 1.

1-*Acetyl*-2-*benzyl*-2-*methoxy*-1,2-*dihydroindol*-3-*one* **2a**. This was prepared from the indolinone **1** (0.21 g, 1 mmol) and benzyl bromide (0.86 g, 5 mmol) in 72% yield (0.21 g), m.p. 101–103 °C (from diethyl ether–hexane) (Found: C, 73.15; H, 5.8; N, 4.65. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%); δ(60 MHz; $CDCl_3$) 2.58 (3 H, s, COMe), 3.18 (3 H, s, OMe), 3.43 (2 H, s, CH_2), 6.65–7.7 (8 H, m, ArH) and 8.38 (1 H, d, *J* 8, ArH); *m/z* 295 (M^+, 2%), 204 (37), 162 (100) and 91 (22).

1-*Acetyl*-2-*methoxy*-2-(3-*methylbut*-2-*enyl*)-1,2-*dihydroindol*-3-*one* **2b**. This was prepared from the indolinone **1** (0.31 g, 1.5 mmol) and 3-methylbut-2-enyl bromide (1.12 g, 7.5 mmol) in 96% yield (0.40 g), b.p. 67–72 °C at 0.2 mmHg (bath temp.) (Found: M^+, 273.1379. $C_{16}H_{19}NO_3$ requires *M*, 273.1365); δ(60 MHz; $CDCl_3$) 1.45 (3 H, s, Me), 1.55 (3 H, s, Me), 2.50 (3 H, s, COMe), 2.88 (2 H, d, *J* 8, CH_2C=), 3.13 (3 H, s, OMe), 4.65 (1 H, t, *J* 8, CH=), 7.18 (1 H, t, *J* 7, ArH), 7.5–7.95 (2 H, m, ArH) and 8.63 (1 H, d, *J* 9, ArH); *m/z* 273 (M^+, 0.2%), 241 (23), 204 (19) and 162 (100).

1-*Acetyl*-2-*allyl*-2-*methoxy*-1,2-*dihydroindol*-3-*one* **2c**. This was prepared from the indolinone **1** (0.31 g, 1.5 mmol) and allyl bromide (0.91 g, 7.5 mmol) in 76% yield (0.28 g), b.p. 70 °C at 0.2 mmHg (bath temp.) (Found: C, 68.4; H, 6.15; N, 5.6. $C_{14}H_{15}NO_3$ requires C, 68.55; H, 6.15; N, 5.7%); δ(60 MHz; $CDCl_3$) 2.47 (3 H, s, COMe), 2.92 (2 H, d, *J* 6, CH_2C=), 3.12 (3 H, s, OMe), 4.7–5.35 (3 H, m, CH=CH_2), 7.10 (1 H, t, *J* 8, ArH), 7.60 (1 H, t, *J* 8, ArH), 7.65 (1 H, t, *J* 8, ArH) and 8.55 (1 H, d, *J* 8, ArH); *m/z* 245 (M^+, 2%), 204 (42), 162 (100) and 43 (32).

1-*Acetyl*-2-*methoxy*-2-[1-(4-*pyridyl*)*ethyl*]-1,2-*dihydroindol*-3-*one* **2d**. This was prepared from the indolinone **1** (0.21 g, 1 mmol) and 1-(4-pyridyl)ethyl bromide hydrobromide (0.50 g, 1.9 mmol) in 55% yield (0.17 g), m.p. 173–174 °C (from diethyl ether–hexane) (Found: C, 69.7; H, 5.8; N, 8.95. $C_{18}H_{18}N_2O_3$ requires C, 69.65; H, 5.85; N, 9.05%); δ(60 MHz; $CDCl_3$) 1.62 (3 H, d, *J* 7, Me), 2.55 (3 H, s, COMe), 3.23 (3 H, s, OMe), 3.77 (1 H, q, *J* 7, CH), 6.8–7.7 (5 H, m, ArH) and 8.3–8.45 (3 H, m, ArH); *m/z* 310 (M^+, 4%), 204 (33) and 162 (100).

1-*Acetyl*-2-*methoxy*-2-*methyl*-1,2-*dihydroindol*-3-*one* **2e**. *Procedure A*. This was prepared from the indolinone **1** (53 mg, 0.26 mmol) and methyl iodide (1 cm^3) in 7% yield (4 mg). The structure was identified by direct comparison of the spectral data with that of an authentic sample.[6]

Procedure B. A solution of the indolinone **1** (53 mg, 0.26 mmol) in dry tetrahydrofuran (THF) (1 cm^3) was added to a suspension of NaH (50%; 24 mg, 0.5 mmol) in dry THF (1.5 cm^3) at room temperature. After 0.5 h, further methyl iodide (0.2 cm^3) was added to the mixture at the same temperature. After being stirred for 1 h the reaction mixture was extracted with ethyl acetate (50 cm^3). The extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give a residue. The residue was purified by PLC on silica gel with CH_2Cl_2–ethyl acetate (50:1) as developing solvent to give the indolinone **2e** (30 mg, 52%).

1-*Acetyl*-2-(2-*cyanoethyl*)-2-*methoxy*-1,2-*dihydroindol*-3-*one* **2f**. *Procedure C*. A solution of the indolinone **1** (1.26 g, 6.15 mmol), acrylonitrile (1.96 g, 37 mmol), and triethylamine (1.45 g, 14.5 mmol) in Bu^tOH (18 cm^3) was refluxed for 93 h. The reaction mixture was evaporated under reduced pressure to give an oily residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (4:1) gave the *alkylated product* **2f** (0.62 g, 39%), m.p. 105–106 °C (from diethyl ether–ethyl acetate) (Found: C, 65.05; H, 5.35; N, 10.75. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.45; N, 10.85%); δ(60 MHz; $CDCl_3$) 2.0–2.35 (4 H, m, CH_2CH_2), 2.47 (3 H, s, COMe), 3.13 (3 H, s, OMe), 7.13 (1 H, t, *J* 8, ArH), 7.45–7.85 (2 H, m, ArH) and 8.50 (1 H, d, *J* 9, ArH); *m/z* 258 (M^+, 37%), 215 (100), 201 (51), 188 (48) and 183 (62).

General Procedure for the Reduction of 2-*Alkyl*-2-*methoxy*-1,2-*dihydroindol*-3-*ones* **2a–c**, **2f** *and the Indolinone* **1** *with Sodium Borohydride*.—Sodium borohydride (10 mmol) was gradually added to a solution of the indolinone **2** or **1** (1 mmol) in MeOH (7 cm^3) at 0–5 °C. After 0.5–1 h, the reaction mixture was concentrated under reduced pressure to give a residue, which was extracted with CH_2Cl_2 (100 cm^3). The extract was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to give the corresponding 3-hydroxy-2-methoxy-2,3-dihydroindole **4**. The ^1H NMR spectral data (400 MHz) of the products **4a–c** and **4f** are shown in Table 3.

1-*Acetyl*-2-*benzyl*-2-*methoxy*-2,3-*dihydroindol*-3-*ol* **4a**. This was prepared from the indolinone **2a** (0.62 g, 2.1 mmol) in 99% yield (0.62 g), m.p. 125–127 °C (from Et_2O) (Found: C, 72.6; H, 6.4; N, 4.7. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%); ν_{max}($CHCl_3$)/cm^{-1} 3450 and 1658; *m/z* 297 (M^+, 4%), 265 (51), 222 (30), 206 (36), 164 (64) and 132 (100).

1-*Acetyl*-2-*methoxy*-2-(3-*methylbut*-2-*enyl*)-2,3-*dihydroindol*-3-*ol* **4b**. This product, which was a mixture of *trans* and *cis*-isomers in the ratio of 1:1.6, was prepared from the indolinone **2b** (1.55 g, 5.7 mmol) in 96% yield (1.50 g) as a viscous oil (Found: M^+, 275.1498. $C_{16}H_{21}NO_3$ requires *M*, 275.1522). Further, the *trans* and *cis* isomers were separated from a part of this mixture by PLC on silica gel with CH_2Cl_2–ethyl acetate (20:1) as developing solvent; *trans*-isomer, ν_{max}($CHCl_3$)/cm^{-1} 3460 and 1661; *m/z* 275 (M^+, 5%), 243 (35), 206 (68), 164 (97) and 132 (100); and *cis*-isomer, ν_{max}($CHCl_3$)/cm^{-1} 3460 and 1669; *m/z* 275 (M^+, 0.6%), 243 (30), 175 (61) and 133 (100).

1-*Acetyl*-2-*allyl*-2-*methoxy*-2,3-*dihydroindol*-3-*ol* **4c**. This *compound* which was a mixture of *trans*- and *cis*-isomers in the ratio of 1:3.2, was prepared from the indolinone **2c** (0.20 g, 0.8 mmol) in 90% yield (0.18 g) as a viscous oil (Found: M^+, 247.1234. $C_{14}H_{17}NO_3$ requires *M*, 247.1209); ν_{max}($CHCl_3$)/cm^{-1} 3440 and 1667; *m/z* 247 (M^+, 18%), 206 (61), 172 (54), 164 (57) and 132 (100).

1-*Acetyl*-2-(2-*cyanoethyl*)-2-*methoxy*-2,3-*dihydroindol*-3-*ol* **4f**. This was prepared from the indolinone **2f** (0.28 g, 1.1 mmol) in 96% yield (0.27 g), m.p. 158–161 °C (from EtOAc) (Found: C, 64.4; H, 6.2; N, 10.7. $C_{14}H_{16}N_2O_3$ requires C, 64.6; H, 6.2; N, 10.75%); ν_{max}($CHCl_3$)/cm^{-1} 3300, 2260 and 1632; *m/z* 260 (M^+, 19%), 217 (49), 185 (100) and 158 (36).

1-*Acetyl*-2-*methoxy*-2,3-*dihydroindol*-3-*ol* **4g**. This was prepared from the indolinone **1** (1.13 g, 5.5 mmol) in 90% yield (1.03 g), m.p. 120–122 °C (from Et_2O) (lit.,[15] 121–122 °C). The spectral data were identical with those of an authentic sample.[15]

General Procedure for the Demethoxylation of the 2,3-*Dihydroindoles* **4a–c** *and* **4f**.—(i) *With tin*(IV) *chloride*. To a solution of the indole **4** (1 mmol) in CH_2Cl_2 (13 cm^3) at 0 °C was gradually added anhydrous tin(IV) chloride (1.3 mmol) and the mixture was then stirred for 0.5–1 h at the same temperature, and was then extracted with CH_2Cl_2 (30 cm^3). The extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give a residue, which was chromatographed on a silica gel column with CH_2Cl_2 (for **5a**), CH_2Cl_2–ethyl acetate (30:1, for **5f**), or hexane–ethyl acetate (3:1, for **6**) to give the corresponding 2-alkylindolinone **5a**, **5f**, or pyranoindole **6**.

1-*Acetyl*-2-*benzyl*-1,2-*dihydroindol*-3-*one* **5a**. This was prepared from the indole **4a** (0.93 g, 3.1 mmol) with tin(IV) chloride (1.10 g, 4.2 mmol) in 64% yield (0.53 g), m.p. 81–83 °C (from Et_2O–EtOAc) (lit.,[10] 120 °C) (Found: C, 76.8; H, 5.55; N, 5.25. $C_{17}H_{15}NO_2$ requires C, 76.95; H, 5.7; N, 5.3%); ν_{max}($CHCl_3$)/cm^{-1} 1724 and 1676; δ (60 MHz; $CDCl_3$) 1.90 (3 H, d, COMe), 3.40 (2 H, d, *J* 5, CH_2), 4.53 (1 H, t, *J* 5, CH), 6.9–7.8 (8 H, m, ArH) and 8.10 (1 H, br d, *J* 8, ArH); *m*/*z* 265 (M^+, 55%), 222 (20), 132 (100) and 91 (58).

1-*Acetyl*-2-(2-*cyanoethyl*)-1,2-*dihydroindol*-3-*one* **5f**. This was prepared from the indole **4f** (0.27 g, 1 mmol) and tin(IV) chloride (0.29 g, 1.1 mmol) in 93% yield (0.22 g), b.p. 198 °C at 0.2 mmHg (bath temp.) (Found: M^+, 228.0901. $C_{13}H_{12}N_2O_2$ requires *M*, 288.0898); ν_{max}($CHCl_3$)/cm^{-1} 2250, 1722 and 1680; δ(60 MHz; $CDCl_3$) 2.1–2.75 (4 H, m, CH_2CH_2), 2.43 (3 H, s, COMe), 4.37 (1 H, t, *J* 5, CH), 7.10 (1 H, t, *J* 8, ArH), 7.58 (1 H, t, *J* 8, ArH), 7.65 (1 H, d, *J* 8, ArH) and 7.97 (1 H, d, *J* 8, ArH); *m*/*z* 228 (M^+, 26%), 186 (100) and 158 (33).

5-*Acetyl*-2,2-*dimethyl*-2,3,4,5-*tetrahydropyrano*[3,2-b]*indole* **6**. This was prepared from the indole **4b** (0.80 g, 2.9 mmol) and tin(IV) chloride (1.00 g, 3.8 mmol) in 16% yield (0.11 g), m.p. 106–109 °C (from diethyl ether–hexane) (Found: C, 74.0; H, 7.1; N, 5.7. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05; N, 5.75%); ν_{max}($CHCl_3$)/cm^{-1} 1690 and 1636; δ(60 MHz; $CDCl_3$) 1.37 (6 H, s, 2 × Me), 1.82 (2 H, t, *J* 7, CH_2), 2.58 (3 H, s, COMe), 3.00 (2 H, t, *J* 7, CH_2), 7.0–7.7 (3 H, m, ArH) and 7.85–8.2 (1 H, br, ArH); *m*/*z* 243 (M^+, 52%), 201 (20) and 145 (100).

(ii) *With trimethylsilyl* (*TMS*) *triflate*. To a solution of an indole **4** (1.8 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C was gradually added TMS triflate (2.3 mmol). The reaction mixture was stirred at the same temperature for 0.5 h, and then evaporated under reduced pressure to give a residue. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (3:1) as eluent to give the corresponding 2-alkylindolinone **5**.

1-*Acetyl*-2-(3-*methylbut*-2-*enyl*)-1,2-*dihydroindol*-3-*one* **5b**. This was prepared from the indole **4b** (0.50 g, 1.8 mmol) and TMS triflate (0.52 g, 2.3 mmol) in 81% yield (0.28 g), b.p. 155–160 °C at 0.2 mmHg (bath temp.) (Found: M^+, 243.1281. $C_{15}H_{17}NO_2$ requires *M*, 243.1259); ν_{max}($CHCl_3$)/cm^{-1} 1724 and 1680; δ(60 MHz; $CDCl_3$) 1.58 (6 H, s, 2 × Me), 2.40 (3 H, s, COMe), 2.50 (2 H, br t, CH_2), 4.37 (1 H, t, *J* 5, CH), 4.90 (1 H, t, *J* 7, =CH), 7.17 (1 H, t, *J* 8, ArH), 7.63 (1 H, t, *J* 8, ArH), 7.72 (1 H, d, *J* 8, ArH) and 8.35 (1 H, d, *J* 8, ArH); *m*/*z* 243 (M^+, 23%), 175 (56) and 133 (100).

1-*Acetyl*-2-*allyl*-1,2-*dihydroindol*-3-*one* **5c**. This was prepared from the indole **4c** (0.15 g, 0.6 mmol) and TMS triflate (0.175 g, 0.79 mmol) in 77% yield (0.10 g), m.p. 92–94 °C (from cyclohexane) (Found: C, 72.2; H, 6.05; N, 6.4. $C_{13}H_{13}NO_2$ requires C, 72.55; H, 6.1; N, 6.5%); ν_{max}($CHCl_3$)/cm^{-1} 1720 and 1676; δ(60 MHz; $CDCl_3$) 2.33 (3 H, s, COMe), 2.83 (2 H, t, *J* 5, CH_2), 4.27 (1 H, t, *J* 5, CH), 4.8–5.9 (3 H, m, CH=CH_2), 7.10 (1 H, t, *J* 8, ArH), 7.57 (1 H, t, *J* 8, ArH), 7.65 (1 H, d, *J* 8, ArH) and 8.30 (1 H, d, *J* 8, ArH); *m*/*z* 215 (M^+, 23%), 172 (13), 144 (24) and 132 (100).

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