ATTEMPTED INTRAMOLECULAR POLONOVSKI CYCLISATION OF AN INDOLE-LINKED QUINUCLIDINE DERIVATIVE - A NOVEL INTRAMOLECULAR OXYGEN TRANSFER REACTION

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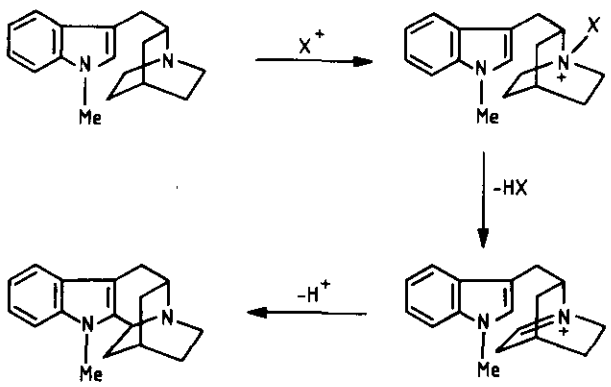
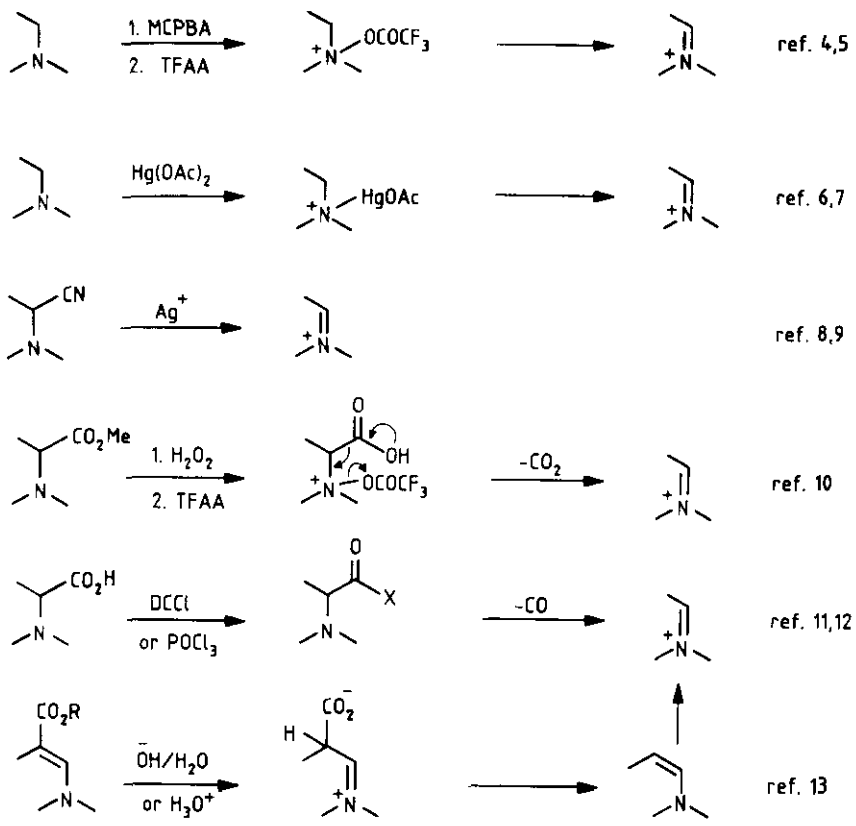
Abstract — *An attempted modified Polonovski reaction on the indole-linked quinuclidine 8 resulted in formation of the amide 10 by transfer of an oxygen atom from the quinuclidine N to the indole C-2 position.*

In an attempt to devize a new route to compounds containing the sarpagine/ajmaline skeleton[1-3] we were attracted by the possibility of carrying out an intramolecular iminium ion cyclization involving an indole-linked quinuclidine as outlined in Scheme 1. Various methods which have been used to generate such iminium ions are shown in Scheme 2.[4-13] Such reactions, including the modified Polonovski reaction,[5,14] have been widely used to bring about cyclization of indole derivatives.[15-20] This would however be the first reported attempt to bring about such a reaction involving a quinuclidine system.



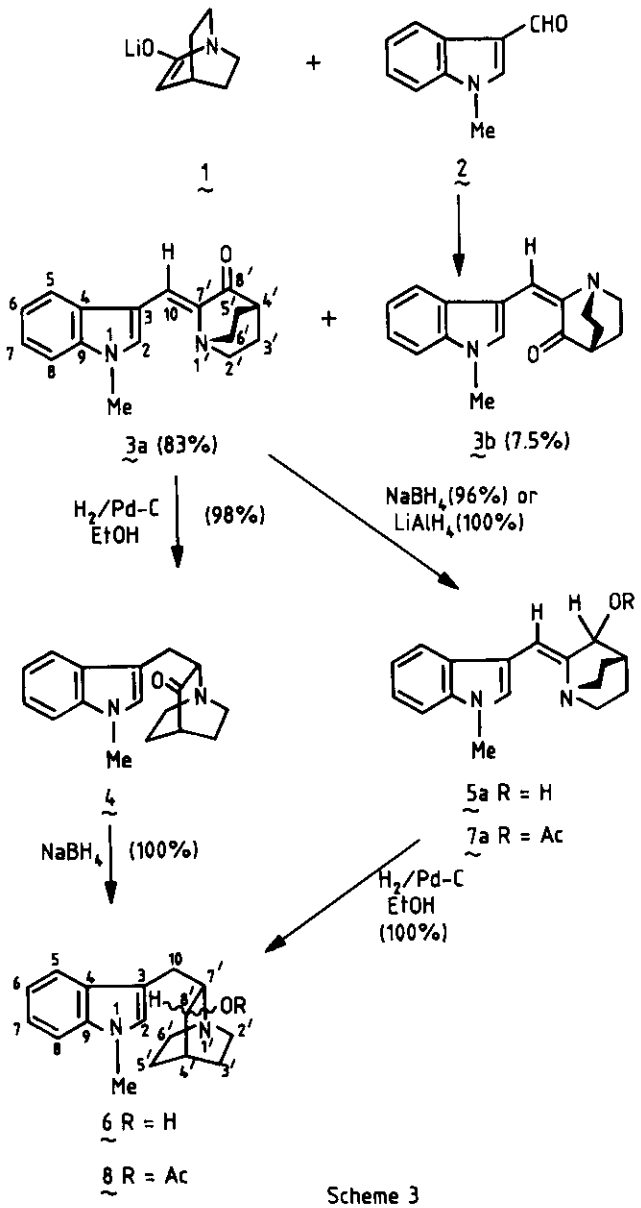
Scheme 1

Generation of Iminium Ions



Scheme 2

The $\alpha\beta$-unsaturated indole-quinuclidinone 3 was prepared by reacting the lithium enolate 1 of quinuclidinone with N-methyl-indole-3-carboxaldehyde 2. Work-up followed by flash chromatography afforded the major isomer 3a (83%) along with the minor isomer 3b (7.5%). Furthermore the major product 3a could be quantitatively converted into its isomer 3b by treatment with titanium tetrachloride. The ^{1}H and ^{13}C n.m.r. spectra are listed in Tables 1 and 2. Of particular importance was the assignment of H-2 and H-10 which both appeared as singlets in the ^{1}H n.m.r. spectrum but could be distinguished on the basis of the Nuclear Overhauser Enhancement of H-2 observed on irradiation of the indole N-methyl signal. The marked difference in the chemical shift of H-2 in 3a and 3b was used to assign the relative

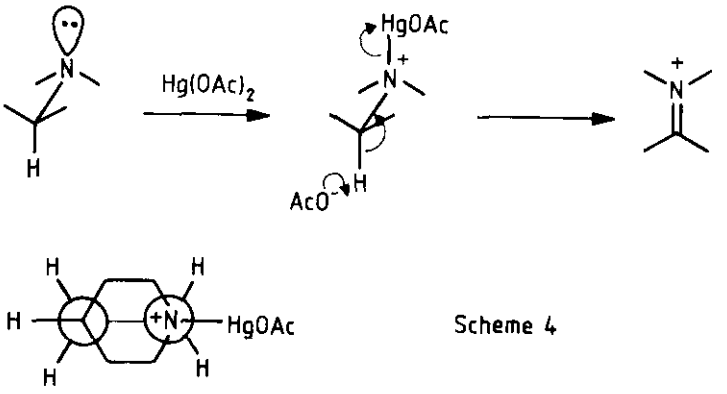

LiO
CHO
Me
1
2
3a (83%)
3b (7.5%)
H2/Pd-C
EtOH
(98%)
NaBH4(96%) or
LiAlH4(100%)
4
5a R = H
7a R = Ac
NaBH4
(100%)
H2/Pd-C
EtOH
(100%)
6 R = H
8 R = Ac

Scheme 3

configuration of the two isomers. Thus it is apparent that the close proximity of the carbonyl group to H-2 in isomer 3b has a marked deshielding effect, while the N lone pair may have a shielding effect on H-2 in 3a. In the minor isomer 3b H-2 is observed at δ9.0 p.p.m. whereas in the major isomer 3a it comes at δ8.2 p.p.m.

Hydrogenation of 3a afforded the saturated ketone 4 ($\nu_{C=O}$ 1730 cm^{-1}) while $NaBH_4$ or $LiAlH_4$ reduction gave the allylic alcohol 5a. Hydrogenation of 5a or $NaBH_4$ reduction of 4 afforded the saturated alcohol 6 which was available therefore in 96-100% yield from 3a (Scheme 3).

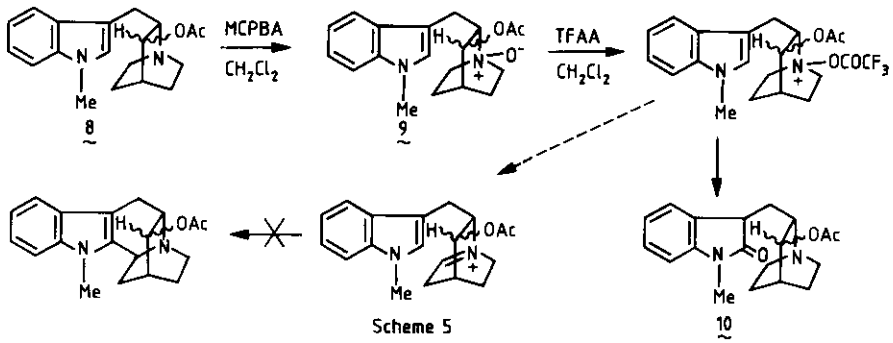
Preliminary attempts to cyclize 4 and 6 using mercuric acetate were unsuccessful. In both cases the only product obtained after sodium borohydride work-up was the saturated alcohol 6. Difficulty in achieving the required cyclization was not unexpected since it requires the generation of a bridgehead iminium ion (see Scheme 1). Furthermore, it has been previously shown that decomposition of the amino-mercuric acetate complex to form an iminium ion only occurs readily when the N lone pair in the starting amine and the α-hydrogen eliminated can adopt a trans-coplanar arrangement (Scheme 4).[21] The rigidity of the quinuclidine system clearly precludes such an arrangement.



Scheme 4

Similar problems might also be anticipated in using the modified Polonovski reaction. Thus the intermediate iminium ion would contain a bridgehead C-N double bond, while formation of this ion would be expected to be more favourable when the proton α to nitrogen is trans-coplanar to the trifluoroacetate group. Nevertheless the indole-quinuclidinol acetate was converted into its N-oxide by refluxing with meta-chloroperoxybenzoic acid in dichloromethane. After purification of the crude product by filtration through a column of alumina the N-oxide 9 was obtained in 90% yield (Scheme 5). Both the ^1H and ^{13}C n.m.r. spectra of 9 (Tables 1 and 2) were similar to those of the starting amine 8, the most noticeable differences

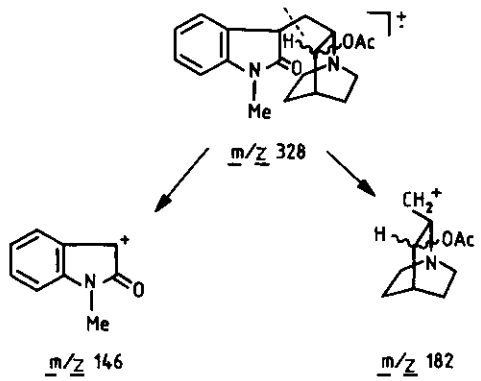
being found for those protons and carbons close to the quinuclidine nitrogen. The mass spectrum of 9 contained a molecular ion at m/z 328 and in addition gave major fragment ions at m/z 312 (M-O) and 269 (M-OAc).



8 9 10

Scheme 5

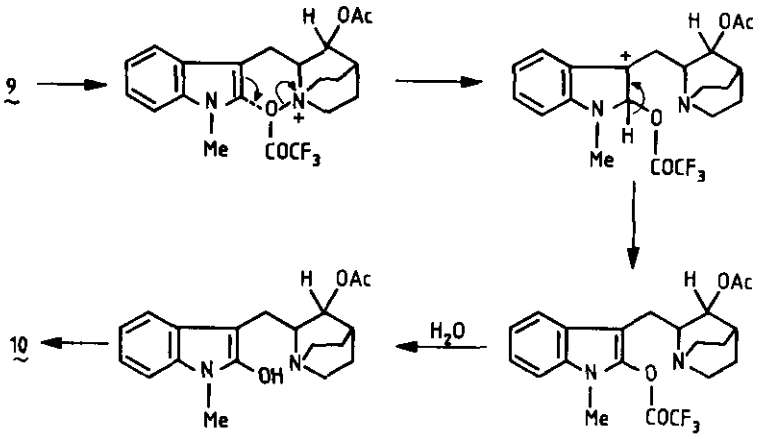
The N-oxide 9 was stirred with trifluoroacetic anhydride in dichloromethane for 3 h, after which the solvent and excess anhydride were evaporated off. The crude reaction mixture was then treated with aqueous KCN in order to trap any uncyclized iminium ions. After work-up in the usual way followed by flash chromatography one major product, identified as the amide 10, was isolated in 40% yield. The mass spectrum of 10 contained a molecular ion at m/z 328, as did the N-oxide 9. However, the fragmentation pattern showed many differences, major fragment ions being found at m/z 285 (M-Ac), 269 (M-OAc), 182 and 146. The latter two ions were regarded as particularly diagnostic since they correspond to cleavage of the molecule into two halves (Scheme 6)



Scheme 6

Both the ^1H and ^{13}C n.m.r. spectra of 10 were complicated, with the ^{13}C n.m.r. spectrum containing several sets of peaks. This was not unexpected since there are now three chiral

centres at C-3, C-7' and C-8'. Of particular interest were the signals at δ 177.81, 178.16 and 178.51 which are characteristic of the C-2 carbonyl group.[22] Other characteristic signals were found at δ 42.44, 42.65, 42.76 (C-3), 59.78, 60.13 (C-7'), 71.78, 72.07 (C-8') and 170.49, 170.67 (acetate C=O). A possible mechanism for the formation of 10 is shown in Scheme 7.



Scheme 7

EXPERIMENTAL

IR Spectra were recorded on a Pye Unicam SP150 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian HA100 and XL100 instruments using TMS as internal standard. 360 MHz NMR spectra were provided by the Edinburgh University WH-360 NMR service. Mass spectra were recorded on an A.E.I. MS9 double focussing instrument at 250°C and 70 eV. THF was distilled over calcium hydride and stored under N_2. CH_2Cl_2 was passed down an alumina column and distilled. Column chromatography was carried out with Merck 7734 silica and flash chromatography with Merck 9385 silica.

N-Methylindole-3-carboxaldehyde (2).

To a stirred suspension of NaH (4.8g, 150 mmol) in THF (100 ml) at 0°C, under N_2, was added a solution of indole-3-carboxaldehyde (20g, 138 mmol) in THF (250 ml), followed by MeI (28.4 ml, 300 mmol), and the mixture stirred overnight at room temperature. Excess hydride was then destroyed by addition of MeOH/H_2O and the mixture extracted with $CHCl_3$ (3 x 150 ml). The combined organic layers were dried over Na_2SO_4 and evaporated to give an orange-coloured solid (19.68g) which was recrystallized from benzene/petroleum ether (bp 40-60°C) to give 2 (17.2g, 80% yield) as cream-coloured crystals, mp 60-63°C, IR 1650 cm^{-1}, MS m/z (rel.int.) 159 (M^+, 79.2%), 158 (100%), 103 (12.4%), 77 (15.9%). Found (calc. for $C_{10}H_9NO$) C, 75.60% (75.45), H, 5.76% (5.70), N, 8.70% (8.80).

Condensation of N-Methylindole-3-carboxaldehyde (2) and 3-Quinuclidinone Hydrochloride.

To a stirred solution of diisopropylamine (19.23g, 190 mmol) in THF (200 ml) at 0°C under N_2 was added a solution of 2.09M n-butyllithium (90 ml, 188 mmol) and the mixture stirred at this temperature for 30 min. To this solution, at 0°C, was added 3-quinuclidinone.HCl (15.0g, 92.8 mmol) in one lot, and stirring continued until completely dissolved (20 min). The temperature was then lowered to -78°C and a solution of 2 (14.6g, 92 mmol) in THF (250 ml) added. Stirring was continued for 30 min at this temperature and then at 0°C for 90 min. The reaction mixture was poured into saturated $NaHCO_3$ at 0°C and this solution extracted with $CHCl_3$ (3 x 150 ml). The combined organic layers were dried over Na_2SO_4 and evaporated to give a yellow solid. Purification by flash chromatography ($CHCl_3$/2% MeOH) followed by recrystallization from benzene/petroleum ether (bp 40-60°C) afforded 3a (20.3g, 80.3% yield), mp 172-173°C, IR 1610 and 1695 cm^{-1}, MS m/z (rel.int.) 266 (M^+, 100%), 238 (13.3%), 237 (21.0%), 210 (24.9%), 209 (25.3%), 197 (11.4%), 183 (17.4%), 169 (44.0%), 157 (36.9%). Accurate Mass = 266.1419 for $C_{17}H_{18}N_2O$. Found (calc. for $C_{17}H_{18}N_2O$) C, 76.40% (76.66), H, 7.00% (6.81), N, 10.39% (10.52).

Increasing the flash chromatography eluent polarity ($CHCl_3$/10% MeOH) led to the recovery of 3b (1.50g, 7.4% yield), IR 1595 and 1695 cm^{-1}, MS m/z (rel. int.) 266 (M^+, 100%), 238 (13.5%), 237 (20.3%), 210 (27.4%), 209 (26.6%), 197 (11.7%), 183 (19.5%), 169 (45.3%), 157 (41.6%), 144 (11.0%).

Catalytic Hydrogenation of 3a.

A solution of 3a (2.50g, 9.40 mmol) in EtOH (40 ml) was hydrogenated over 10% Pd/C for 12 h. The catalyst was removed by repeated filtration and the solvent evaporated to give a brown, fibrous tar which was recrystallized from EtOH to afford 4 (2.50g, 98% yield) as cream-coloured crystals, mp 138°C, IR 1730 cm^{-1}, MS m/z (rel. int.) 268 (M^+, 4.7%), 240 (25.8%), 157 (5.4%), 144 (100%). Accurate mass = 268.1574 for $C_{17}H_{20}N_2O$. Found (calc. for $C_{17}H_{20}N_2O$) C, 75.80% (76.09), H, 7.80% (7.51), N, 10.09% (10.44).

$NaBH_4$/MeOH Reduction of 3a.

To a stirred solution of 3a (2.13g, 8.0 mmol) in MeOH (100 ml) at 0°C was added $NaBH_4$ (3.03g, 80 mmol) over 15 min and stirring continued for 2 h at room temperature. Water (50 ml) was added and the mixture extracted with $CHCl_3$

(3 x 50 ml). The combined organic layers were dried over Na_2SO_4 and evaporated to give 5a as a cream-coloured solid, (2.05g, 96% yield), mp 137°C (from benzene/petroleum ether), IR 3350 cm^{-1}, MS m/z (rel. int.) 268 (M^+, 100%), 252 (12.1%), 184 (15.0%), 170 (20.7%), 169 (28.8%), 168 (17.5%), 144 (59.7%), 131 (24.5%). Found (calc. for $C_{17}H_{20}N_2O$) C, 76.80% (76.09), H, 7.70% (7.51), N, 9.80% (10.44).

$NaBH_4$/MeOH Reduction of 3b.

To a stirred solution of 3b (0.53g, 2.0 mmol) in MeOH (25 ml) at 0°C was added $NaBH_4$ (0.74g, 20 mmol) over 10 min and stirring continued at room temperature for 3 h. Work-up as for 5a afforded 5b, as a cream-coloured solid (0.50g, 93% yield), mp 204-206°C (from EtOH/H_2O), IR 3150 cm^{-1}, MS m/z (rel. int.) 268 (M^+, 100%), 252 (10.6%), 184 (47.6%), 170 (60.8%), 169 (82.3%), 168 (53.0%), 157 (30.3%), 144 (37.9%), 131 (21.1%). Found (Calc. for $C_{17}H_{20}N_2O$) C, 74.42% (76.09), H, 7.40% (7.51), N, 9.98% (10.44).

Isomerization of 3a Using $TiCl_4$.

To a stirred solution of 3a (1.0g, 3.76 mmol) in dry CH_2Cl_2 (10 ml) under N_2 at room temperature was added a solution of $TiCl_4$ (0.49 ml, 4.5 mmol) in CH_2Cl_2 (10 ml) and stirring continued overnight. To the mixture was added ice-water (20 ml), the organic layer removed, washed with saturated NaCl (3 x 10 ml), saturated $NaHCO_3$ (3 x 10 ml), dried over Na_2SO_4 and evaporated to give a yellow-brown fibrous tar. Purification by flash chromatography afforded 3b (1.0g, 100% yield), which was identified by comparison with the sample obtained by direct condensation (see above).

$LiAlH_4$ Reduction of 3a.

To a solution of 3a (0.70g, 2.63 mmol) in THF (20 ml) at 0°C under N_2 was added a 1.1M solution of $LiAlH_4$ in THF (2.4 ml, 2.63 mmol). The mixture was stirred at this temperature for 1 h and a further 1 h at room temperature. A 1:1 mixture of H_2O/THF was added until H_2 evolution ceased and the solution extracted with CH_2Cl_2 (3 x 10 ml). The combined organic layers were washed with saturated $NaHCO_3$ (3 x 10 ml), H_2O (2 x 10 ml), dried over $MgSO_4$ and evaporated to give 5a as a cream-coloured solid (0.70g, 100% Yield), which was identical to the sample prepared using $NaBH_4$/MeOH (see above).

$NaBH_4$ Reduction of 3a in Refluxing Ethanol.

To a solution of 3a (0.50g, 1.87 mmol) in dry EtOH (10 ml) was added $NaBH_4$ (0.38g, 10 mmol) at room temperature and the mixture stirred at this temperature for 30 min. This was then gently refluxed for 1 h, after which H_2O (10 ml) was added, followed by saturated $NaHCO_3$ (10 ml). The mixture was extracted with CH_2Cl_2 (3 x 10 ml), the combined organic layers dried over Na_2SO_4 and evaporated to afford 5a as a cream-coloured solid (0.48g, 95% yield), which was identified by comparison with the sample prepared in MeOH at room temperature (see above).

$NaBH_4$/MeOH Reduction of 4.

To a stirred solution of 4 (0.55g, 2.96 mmol) in MeOH (20 ml) at 0^oC was added $NaBH_4$ (0.38g, 10 mmol) and stirring continued at room temperature for 3 h. Water (20 ml) was then added and the mixture extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, dried over $MgSO_4$ and evaporated to give a pale yellow solid (0.55g, 100%) which gave a single spot by TLC and proved to be the alcohol 6, IR 3240 cm^{-1}, MS m/z (rel. int.) 270 (M^+, 43.0%), 213 (18.9%), 158 (12.5%) (17.6%), 144 (100%), 131 (21.8%), 126 (25.4%).

Catalytic Hydrogenation of 5a.

A solution of 5a (4.03g, 15.0 mmol) in EtOH (40 ml) was hydrogenated over 10% Pd/C overnight. The catalyst was removed by repeated filtration and the solvent evaporated to leave 8 (4.05g, 100% yield) as a pale cream solid, identical to the sample prepared above.

Attempted Mercuric Acetate Cyclization of 4.

To a solution of $Hg(OAc)_2$ (3.03g, 9.5 mmol) and EDTA $Na_2.2H_2O$ (3.70g, 10.0 mmol) in H_2O (20 ml) was added a solution of 4 (0.5g, 1.87 mmol) in CH_2Cl_2 (10 ml). The CH_2Cl_2 was evaporated off by passing N_2 through the mixture while stirring at 40^oC. The pH was adjusted to 7.0 by addition of aqueous 1N NaOH and the mixture refluxed for 35 min before cooling and basifying with 1N NaOH. EtOH (20 ml) was added followed by $NaBH_4$ (0.8g, 21 mmol) and the mixture stirred for 30 min at room temperature before filtering. The filtrate was concentrated and then extracted with CH_2Cl_2 (3 x 15 ml). The combined organic layers were dried over $MgSO_4$ and evaporated to give 8 (0.45g, 93% yield).

Attempted Mercuric Acetate Cyclization of 6.

To a stirred solution of 6 (0.29g, 1.07 mmol) in glacial AcOH (10 ml) was added $Hg(OAc)_2$ (0.96g, 3 mmol) and stirring continued for 24 h at room temperature under N_2. A small amount of solid material was filtered off (0.17g), the filtrate refluxed for 6 h, cooled, and the AcOH evaporated off under reduced pressure. EtOH (20 ml) was added, followed by treatment with $NaBH_4$ (1.0g, 26 mmol) at 0^oC, and stirring continued at room temperature for 1 h. The mixture was filtered, the filtrate treated with H_2O (20 ml) and extracted with $CHCl_3$ (3 x 15 ml). The combined organic layers were dried over $MgSO_4$ and evaporated to give a pale brown solid (0.26 g) which contained mainly unreacted starting material.

Acetylation of 5a.

A solution of 5a (0.5g, 1.86 mmol) in pyridine (2 ml) and acetic anhydride (1 ml) was stirred overnight at room temperature under N_2. The mixture was poured into ice-water (80 ml) and left to stand for 30 min before extracting with CH_2Cl_2 (3 x 30 ml). The combined organic layers were washed with 1N HCl (2 x 30 ml), $NaHCO_3$ (2 x 30 ml), H_2O (2 x 30 ml), dried over $MgSO_4$ and evaporated to give a pale orange solid. Purification by flash chromatography ($CHCl_3$/2% MeOH) afforded 7a (0.40g, 66% yield), IR 1660 cm^{-1}, MS m/z (rel. int.) 310 (M^+, 40%), 267 (12%), 251 (100%), 250 (41%), 169 (20%), 144 (25%), 43 (35%). Accurate mass = 310.1681 for $C_{19}H_{22}N_2O_2$.

Acetylation of 6.

A solution of 6 (2.4g, 8.9 mmol) in pyridine (10 ml) and acetic anhydride (5 ml) was stirred overnight at room temperature under N_2. The mixture was poured into ice-water (150 ml) and stirred for a further 30 min. This was then extracted with CH_2Cl_2 (3 x 50 ml), the combined organic layers washed with 1N HCl (2 x 50 ml), $NaHCO_3$ (2 x 50 ml), H_2O (2 x 50 ml), dried over $MgSO_4$ and evaporated to give a brown oil. Purification by flash chromatography ($CHCl_3 \rightarrow CHCl_3$/20% MeOH) yielded 8 as an oil (1.20g, 43%), IR 1740 cm^{-1}, MS m/z (rel. int.) 312 (M^+, 45.4%), 269 (100%), 158 (45.2%), 144 (63.1%).

Indole-quinuclidine N-Oxide (9).

To a solution of 8 (1.30g, 4.17 mmol) in CH_2Cl_2 (20 ml) was added mCPBA (1.56g, .9 mmol) in CH_2Cl_2 (40 ml) over 15 min, while gently refluxing. After a further 30 min stirring at room temperature, solid Na_2CO_3 (10 g) was added and stirring was continued for a further 15 min. The mixture was filtered through a bed of Na_2CO_3

and evaporated to give a red/brown solid (1.51 g). The solid was dissolved in CH_2Cl_2 and passed down a short alumina column (CH_2Cl_2/10% MeOH/50 g Al_2O_3). The filtrate was evaporated to afford 9 (1.24g, 90% yield) as an orange-coloured solid. MS m/z (rel. int.) 328 (M^+, 5.7%), 312 (43.3%), 269 (100%), 223 (15.8%), 222 (14.3%), 158 (39.1%), 144 (58.7%).

Treatment of N-Oxide (9) with Trifluoroacetic Anhydride.

To a solution of 9 (0.62g, 1.89 mmol) in CH_2Cl_2 (5 ml) at 0^oC was added TFAA (1 ml) and the mixture stirred at room temperature for 3 h. Solvent and excess TFAA were removed by rotary evaporation without heating and CH_2Cl_2 (10 ml) added, followed, at 0^oC, by KCN (1.30g, 20 mmol) and H_2O (5 ml). The pH was immediately adjusted to 4.0 by trifluoroacetic acid addition and the mixture stirred at room temperature for 30 min. Saturated Na_2CO_3 was added (20 ml) and the mixture extracted with $CHCl_3$ (3 x 20 ml). The combined organic layers were dried over $MgSO_4$ and evaporated to give a brown solid (0.50 g). Purification by flash chromatography afforded 10 as an oil (0.25g, 40% yield), IR 1620, 1730 cm^{-1}, MS m/z (rel. int.) 328 (M^+, 82.4%), 285 (95.2%), 269 (5.9%), 182 (11.6%), 172 (16.7%), 146 (100%), 110 (20.6%), 43 (25.5%). Accurate mass = 146.0596 for C_9H_8NO.

Table 1. ^{1}H NMR Data (in $CDCl_3$ unless otherwise indicated)*

	2	3a	3b	4	5a	5b (MeOH)	6	7a	8	9	10
H-2	7.40s	8.2s	9.0s	6.90s	7.84s	7.80s	7.00s 7.04s	7.90s	6.78s 6.84s	6.78s 6.90s	-
H-3	-	-	-	-	-	-	-	-	-	-	3.50m
H-5	8.5m	9.75m	7.70m	7.61m	7.65m	7.65m	7.75m	7.70m	7.55m	7.70m	6.7-7.3m
H-6/7/8	7.18m	7.2m	7.2m	7.25m	7.10m	7.20m	7.30m	7.15m	7.15m	7.18m	
H-10	9.80s	7.4s	7.17s	3.42m	6.47s	6.90s	2.6-3.6m	6.44s	2.5-3.4m	3.0-3.7m	2.5-3.4m
N-CH_3	3.60s	3.7s	3.70s	3.73s	3.61s	3.90s	3.78s	3.64s	3.60s	3.66s	3.06s 3.10s
H-2') H-6')	-	3.0m(8)	3.05m	2.8-3.3m	2.90m	3.10m	2.95m	2.96m	2.90m	3.55m	2.90m
H-3') H-5')	-	1.93dt(3,8)	1.85m	1.98m	1.50m	1.60m	1.60m	1.60m	1.30m 1.60m	2.0m	1.30m 1.60m
H-4'	-	2.55q(3)	2.64m	2.47m	1.95m	2.15m	1.95m	2.15m	2.0m	2.0m	2.0m
H-7'	-	-	-	2.8-3.3m	-	-	2.6-3.6m	-	2.5-3.4m	3.0-3.7m	2.5-3.4m
H-8'	-	-	-	-	4.30d(2)	4.42d(4)	3.95m	4.50d(2)	4.55m 5.00m	4.90m 5.15m	4.50m 5.00m
OH	-	-	-	-	2.30bs	2.15bs	2.6-3.6m	-	-	-	-
$OCOCH_3$	-	-	-	-	-	-	-	2.05s	1.60s 1.88s	1.40s 1.72s	1.98s 2.02s

* Coupling constants in parentheses.

Table 2. ^{13}C NMR Data (in $CDCl_3$).

	2	3a	3b	4	5a	6	7a	8	9	10		
C-2	139.54	134.82	135.35	127.21	129.88	127.05 126.70	130.32	127.32 126.56	128.13 126.33	178.51	178.16	177.81
C-3	117.82	109.72	109.31	111.35	110.27	112.54 111.52	110.18	111.64 110.78	109.45 107.50	42.76	42.65	42.44
C-4	125.08	128.59	129.29	127.75	127.66	128.07 127.93	127.72	127.94 (x 2)	127.73 127.62	129.39	129.15	128.95
C-5/6/7	121.74	118.89	118.00	118.64	118.50	118.99 118.85	118.56	121.34 (x 2)	119.03 118.77	123.70	123.47	122.88
	123.86	122.47	122.48	121.38	121.43	121.56 121.48	121.60	118.57 118.51	121.75 (x 2)	127.87 124.55	127.76 124.34	123.76
	122.73	120.84	120.92	118.64	119.26	118.71 (x 2)	119.41	118.91 118.68	119.23 119.03	122.30	122.03	121.95
C-8	109.92	109.58	109.74	109.15	109.02	109.11 (x 2)	109.07	109.08 109.00	109.19 109.13	108.23 108.09	107.85	107.79
C-9	137.80	136.60	136.84	136.89	136.12	137.04	136.21	137.06 136.86	137.21 136.84	144.86 144.74	144.30	144.25
C-10	184.28	118.09	125.88	26.58	112.98	25.48 28.92	115.49	28.46 24.81	25.53 23.17	34.18	32.78	
N-CH_3	33.41	33.19	33.25	32.46	32.63	32.43	32.75	32.43 32.35	32.60 32.52	26.16		
C-3'/6'	-	47.62	49.53	48.83	47.78	49.76 48.79	47.49	49.63 48.64	65.26 64.56	49.59	49.42	48.54
				40.92	46.93	41.65 40.77	46.96	41.45 40.72	57.50 56.33	41.10 40.60	41.21 40.77	40.37
C-4'	-	40.55	42.33	40.13	30.93	28.70 28.91	28.05	27.17 26.28	25.97 24.43	27.38 27.20	26.97 26.62	
C-3'/5'	-	26.56	25.69	25.27	25.40	24.64 23.15	24.99	23.77 22.77	22.47 21.33	25.10 24.58	24.43	24.14
				23.64	19.11	18.97 18.63	19.68	19.41 18.95	20.96 17.77	19.67 19.35	19.15	18.97
C-7'	-	140.31	138.10	70.58	146.91	66.57 60.94	141.24	62.79 59.46	73.66 69.61	60.13	59.78	
C-8'	-	205.14	203.11	221.27	71.19	74.05 68.54	73.43	76.23 71.14	75.51 73.90	72.07	71.78	
O<u>C</u>OCH$_3$	-	-	-	-	-	-	171.22	170.31 170.05	169.29 168.99	170.67	170.49	
OCO<u>C</u>H$_3$	-	-	-	-	-	-	21.48	20.82 20.53	20.63 20.02	21.28	21.22	21.04

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