Reduction of 1-(2-Hydroxy-3,5-di-t-butylphenyl)pyridinium Halides and Their Zwitterions. Formation of Di- and Tetra-hydropyrido[2,1-*b*]benzoxazoles[1]

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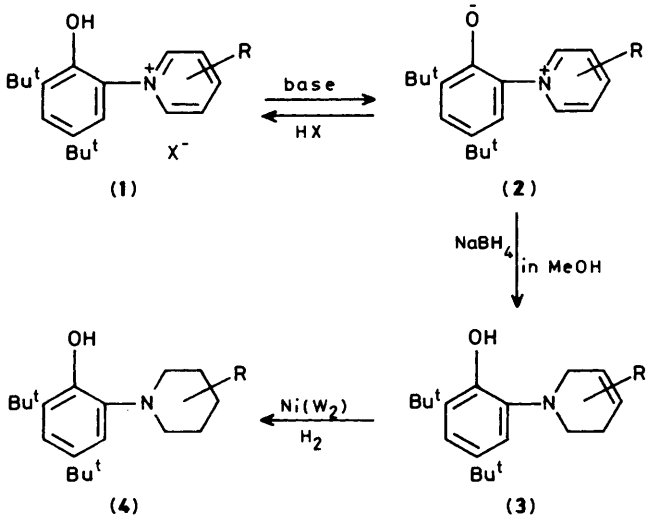
Reduction of 1-(2-hydroxy-3,5-di-t-butylphenyl)pyridinium halides (**1a—d**) and/or their zwitterions (**2a—d**) with Raney Ni–Al alloy, Raney Ni (W_2) and $NaBH_4$ were investigated. When (**1**) was treated with Ni–Al alloy in a mixture of methanol and 30% aqueous KOH, novel cyclization products, 1,2,3,4-tetrahydro- (**5a—d**) and 3,4-dihydro-pyrido[2,1-*b*]benzoxazoles (**6a**) and (**6b**) were obtained. Raney Ni catalyzed hydrogenation of (**1a**), (**1b**), (**2a**), (**2b**), and (**2d**) gave (**5**) and/or 2-piperidinophenols (**4**). Reduction of (**1b**) and (**1d**) with $NaBH_4$ was re-examined and 1,2-dihydro- (**7**) and 1,4-dihydro-pyrido[2,1-*b*]benzoxazole (**8**) were isolated, respectively, as by-products.

It has been reported previously[2] that $NaBH_4$ reduction of 1-(2-hydroxy-3,5-di-t-butylphenyl)pyridinium bromide (**1a—c**) and zwitterion (**2a**) in MeOH afforded a good yield of the (1,2,3,6-tetrahydropyridyl)phenols (**3a—c**), which were easily reduced to the piperidinophenols (**4a—c**) by catalytic hydrogenation with Raney Ni (W_2). De-t-butylation of (**4a**) in 85% H_3PO_4 at 158 °C gave 2-piperidinophenol in a good yield[3] (Scheme 1).



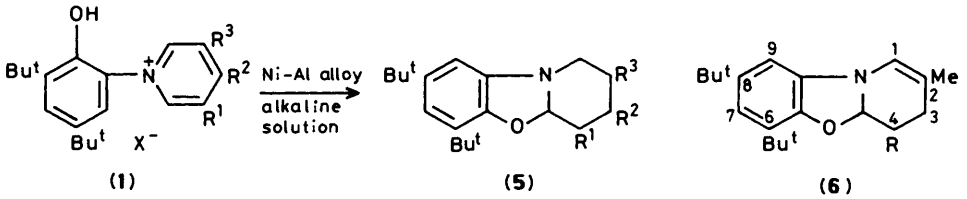
Scheme 1.

To achieve the formation of (**4**) directly from the pyridinium salts (**1**) and/or the zwitterions (**2**), reduction of compounds (**1**) and (**2**) was carried out under the following conditions: (*i*) treatment with Raney Ni–Al alloy in alkaline solution and (*ii*) hydrogenation with Raney Ni (W_2) catalyst. Unexpectedly, a novel reductive cyclization was encountered, giving tetrahydro- (**5**) and dihydro-pyrido[2,1-*b*]benzoxazole (**6**), whose skeletons resemble a part of the structure of vomicine which has a strychnine-like biological activity and is pharmacologically interesting.

The present paper describes the above reduction of compounds (**1**) and (**2**), together with the results of re-investigation of the $NaBH_4$ reduction[2] of the methyl derivative (**1b**) and the dimethyl-substituted derivative (**1d**).

Results and Discussion

Reduction with Raney Ni–Al *Alloy in Alkaline Solution.*— Dissolution of the pyridinium salts (**1a—d**) in a mixture of alcohol and aqueous alkali gave immediate development of an orange-red or violet colour which suggested the formation of the zwitterions (**2a—d**). Treatment of the solution with Raney Ni–Al alloy and termination of the reaction when the mixture became colourless. Although giving none of the expected compounds (**4a—d**) afforded, unexpectedly, the novel cyclization products, tetrahydro- (**5a—d**) and dihydro-pyridobenzoxazoles (**6a—b**) (see Scheme 2 and Table 1). As shown in Table 1 (runs 1—6), optimum conditions were provided by MeOH as a solvent and 30% aqueous KOH as base.



a; $R^1 = R^2 = R^3 = H$, X = Br
b; R^1 = Me, $R^2 = R^3 = H$, X = Br
c; $R^1 = R^3 = H$, R^2 = Me, X = Cl
d; $R^1 = R^3$ = Me, $R^2 = H$, X = Br

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

a: R = H
b: R = Me

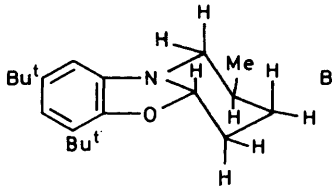
Scheme 2.

Table 1. Reduction of the pyridinium salts (**1**) with Raney Ni–Al alloy in an alkaline solution[a]

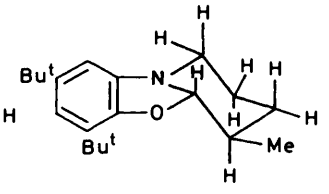
Run	Pyridinium salt	Ni–Al/(1) (w/w)	Solvent (ml)	Aq. alkali (ml)	Time (min)	Product (%)[b]
1	(**1a**)	1.0	EtOH (100)	10% KOH (20)	300	(**5a**) (78)
2	(**1a**)	1.0	EtOH (100)	10% NaOH (20)	300	No reaction
3	(**1a**)	1.0	MeOH (100)	10% KOH (20)	10	(**5a**) (88)
4	(**1a**)	1.0	MeOH (100)	10% NaOH (20)	10	(**5a**) (85)
5	(**1a**)	1.0	MeOH (20)	30% KOH (5)	10	(**5a**) (90)
6	(**1a**)	1.0	MeOH (20)	30% NaOH (5)	10	(**5a**) (60)
7	(**1a**)	0.5	MeOH (20)	30% KOH (5)	10	(**5a**) (89)
8	(**1a**)	0.3	MeOH (20)	30% KOH (5)	10	(**5a**) (69)
9	(**1b**)	1.0	MeOH (20)	30% KOH (5)	10	(**5b**) (34), (**6**) (16)
10	(**1c**)	1.0	MeOH (20)	30% KOH (5)	10	(**5c**) (20)
11	(**1d**)	1.0	MeOH (20)	30% KOH (5)	10	(**5d**) (34), (**7**) (+)

[a] The reaction was carried out at reflux. [b] Isolated yields. Plus sign means less than 1% yield.

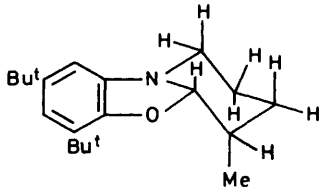
Reduction of (**1a**) gave exclusively (**5a**) in a high yield. Under the same conditions, (**1b**) gave a 6:1 mixture of regioisomers (**5b**-1) and (**5b**-2_1) (34%) accompanied by (**6a**) (16%); a small amount of the stereoisomer (**5b**-2_2) was also observed in the ^{1}H n.m.r. spectrum of this mixture. Compound (**5b**-1) was isolated from this mixture but not (**5b**-2_1) and (**5b**-2_2).



(**5b**-1)

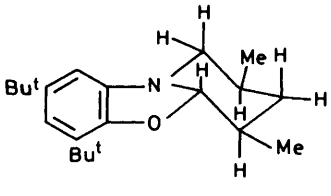


(**5b**-2_1)

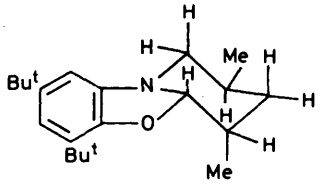


(**5b**-2_2)

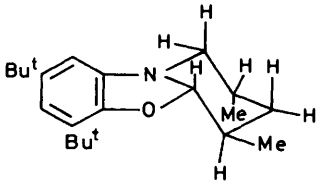
Reduction of (**1c**) gave only (**5c**) (20%) whilst compound (**1d**) gave an 8:1:1 mixture of three stereoisomers (**5d**-1), (**5d**-2), and (**5d**-3) (34%), together with a trace of (**6b**). Compound (**5d**-1) was obtained pure but not (**5d**-2) and (**5d**-3).



(**5d**-1)



(**5d**-2)



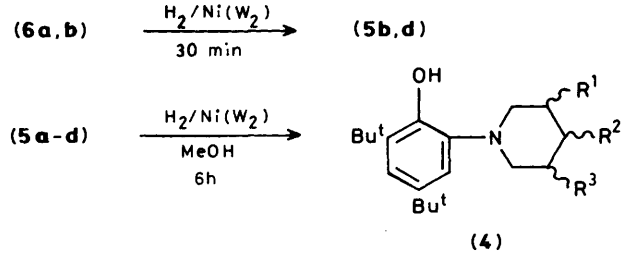
(**5d**-3)

Table 2. Raney Ni (W_2)-catalyzed hydrogenation of compounds (**1**) and (**2**) to afford compounds (**4**) and/or (**5**)

Substrate	Reaction time (h)	Product (%)[a]
(**1a**)	6	(**4a**) (95)
(**1b**)	6	(**4b**) (94)
(**1c**)	6	*b*
(**1d**)	6	(**5d**)[c] (33)[d]
(**2a**)	1/6[e]	(**4a**) (8), (**5a**) (90)
(**2a**)	6	(**4a**) (98)
(**2b**)	1/2[e]	(**4b**) (+), (**5b**)[f] (89)
(**2b**)	6	(**4b**) (96)
(**2c**)[g]	1	(**5c**) (62)[h]
(**2c**)[g]	48	(**4c**) (4), (**5c**) (60)[h]
(**2d**)	1[e]	(**4d**) (10), (**5d**)[c] (70)
(**2d**)	48	(**4d**) (89)

[a] Isolated yield. Plus (+) sign means less than 1%. [b] (**1c**) was recovered quantitatively. [c] An 8:1:1 mixture of (**5d**-1), (**5d**-2), and (**5d**-3) by ^{1}H n.m.r. [d] (**1d**) was recovered in 55% yield. [e] Colour of the reaction mixture changed to pale yellow from dark red at this time. [f] A mixture of 8:1.5:1 of (**5b**-1), (**5b**-2_1) and (**5b**-2_2) by ^{1}H n.m.r. [g] Used without purification because (**2c**) is highly hygroscopic. [h] Yield based on (**1c**).

The dihydro derivatives (**6a**) and (**6b**) were hydrogenated on Raney Ni (W_2) for 30 min, to give the corresponding tetrahydro derivatives (**5b**) and (**5d**) in 60 and 50% yields, respectively. Prolonged reduction of (**5a**—**d**) (6 h), gave ring-cleaved products (**4a**—**d**) (90—99%) (Scheme 3).



(**4**)

a; $R^1 = R^2 = R^3 = H$ (99%)
b; R^1 = Me, $R^2 = R^3 = H$ (95%)
c; $R^1 = R^3 = H$, R^2 = Me (95%)
d; $R^1 = R^3$ = Me, $R^2 = H$ (90%)

Scheme 3.

Reduction with Raney Ni (W_2).—Results for the Raney Ni (W_2)-catalyzed hydrogenation of compound (**1**), and its zwitterion (**2**), in MeOH at room temperature are summarized in Table 2.

(**1**) or (**2**) $\xrightarrow{H_2/Ni(W_2)}$ (**4**) and/or (**5**)

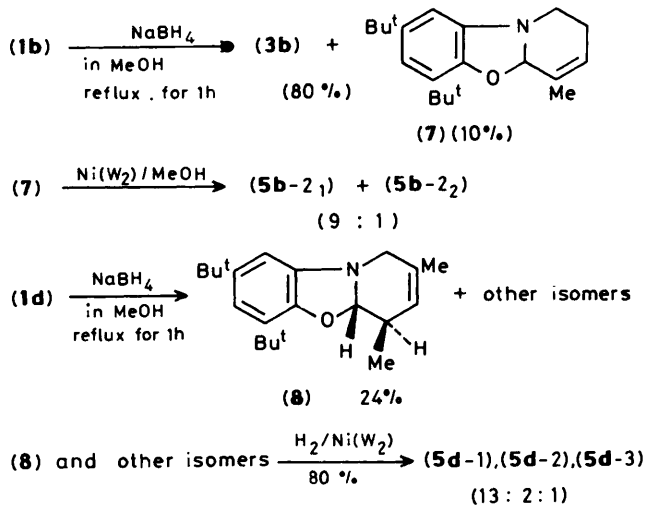
Reduction of compounds (**1a**) and (**1b**) for 6 h gave compounds (**4a**) and (**4b**) respectively in high yields. Compound (**1c**) failed to undergo reduction and was recovered quantitatively. In contrast (**1d**) afforded (**5d**) (33%) as a mixture of three isomers.

Reduction of the zwitterions (**2a**), (**2b**), and (**2d**) gave (**4a**), (**4b**), and (**4d**) and/or (**5a**), (**5b**), and (**5d**) respectively, in yields dependent on the reaction time, as expected; for a prolonged reaction time, formation of ring-opened (**4**) is predominant. Compounds (**5b**) and (**5d**) were obtained as a mixture of isomers. Although reduction of (**2c**) for 1 h gave (**5c**) as the sole product (62%), a 48 h reaction period gave a little of (**4c**) (4%) in addition to (**5c**) (60%). Since (**5c**) was easily hydrogenated to give (**4c**) (95%), this result is both unexplained and seemingly anomalous.

The ratio of isomers (**5b**) and (**5d**) obtained is almost identical with that observed for the Raney Ni–Al alloy reduction of (**1b**) and (**1d**).

Reduction of Compounds (**1b**) *and* (**1d**) *with* $NaBH_4$.—Reduction of (**1a**—**c**) with $NaBH_4$ has already been reported[2] to give (**3a**—**c**). On re-examination of the $NaBH_4$ reduction of (**1b**), (**7**) was isolated as a by-product (10%) together with (**3b**) (80%). Compound (**7**) gave a 9:1 mixture of (**5b**-2_1) and (**5b**-2_2) (60%) on hydrogenation with Raney Ni (W_2) Scheme 4, from which the former was isolated.

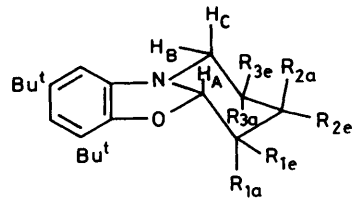
From a complex mixture of the reduction products of (**1d**),[2] (**8**) could be isolated (24%). Catalytic hydrogenation of the above mixture on Raney Ni (W_2) for 1 h afforded a 13:2:1 mixture of (**5d**-1), (**5d**-2), and (**5d**-3) (80%). When the hydrogenation was carried out for 6 h, ring-opened (**4d**) was obtained as reported.[2]



Scheme 4.

Reaction Path.—The reaction path is briefly shown in Scheme 5. The Raney Ni–Al alloy reduction in alkaline solution and Raney Ni (W_2)-catalyzed hydrogenation afforded cyclized dihydro- (**6**) and tetrahydro-pyrido[2,1-*b*]benzoxazoles (**5**)

Table 3. ^{1}H N.m.r. chemical shift (δ p.p.m.) and coupling constants (*J*, Hz) of compound (**5**)



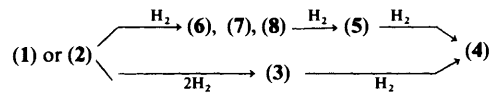
(**5**)

(5)	Substituent R 1a	1e	2a	2e	3a	3e	Bu^t	Aromatic H	H_A	H_B	H_C	Others
a	H	H	H	H	H	H	1.28 (s) 1.36 (s)	6.32 (d) J = 2.5 6.57 (d) J = 2.5	4.98 (dd) $J_{H_A, H_{1a}}$ = 8.0 $J_{H_A, H_{1e}}$ = 3.0	3.44—3.68 (m)	2.74 (ddd) J_{H_C, H_B} = 12.0 $J_{H_C, H_{3a}}$ = 9.0 $J_{H_C, H_{3e}}$ = 5.0	6 H:1.40—2.16 (m)
b-1	H	H	H	H	H	Me	1.27 (s) 1.32 (s)	6.30 (d) J = 2.0 6.56 (d) J = 2.0	5.00 (dd) $J_{H_A, H_{1a}}$ = 9.5 $J_{H_A, H_{1e}}$ = 3.0	3.56 (ddd) J_{H_B, H_C} = 13.0 $J_{H_B, H_{3a}}$ = 4.5 $J_{H_B, H_{2e}}$ = 2.0	2.39 (dd) J_{H_B, H_C} = 13.0 $J_{H_C, H_{3a}}$ = 10.0	Me:0.95 (d) J = 6.0 5 H:1.40—2.16 (m)
b-2_1	H	Me	H	H	H	H	1.28 (s) 1.36 (s)	6.29 (d) J = 2.5 6.55 (d) J = 2.5	4.63 (d) $J_{H_A, H_{1a}}$ = 8.0	3.44—3.75 (m)	2.76 (ddd) J_{H_C, H_B} = 13.0 $J_{H_C, H_{3a}}$ = 8.5 $J_{H_C, H_{3e}}$ = 5.5	Me:1.06 (d) J = 6.0 5 H:1.40—2.00 (m)
b-2_2[a]	Me	H	H	H	H	H	*b*	6.46 (d) J = 2.5 6.62 (d) J = 2.5	4.90 (d) $J_{H_A, H_{1e}}$ = 4.0	*b*	*b*	*b*
c	H	H	H	Me	H	H	1.13 (s) 1.28 (s)	6.32 (d) J = 2.0 6.56 (d) J = 2.0	5.06 (dd) $J_{H_A, H_{1a}}$ = 9.0 $J_{H_A, H_{1e}}$ = 3.0	3.60 (ddd) J_{H_B, H_C} = 12.0 $J_{H_B, H_{3a}}$ = 4.5 $J_{H_B, H_{3e}}$ = 2.0	2.76 (ddd) J_{H_C, H_B} = 12.0 $J_{H_C, H_{3a}}$ = 12.0 $J_{H_C, H_{3e}}$ = 3.0	Me:1.00 (d) J = 6.0 5 H:1.42—1.72 (m)
d-1	H	Me	H	H	H	Me	1.27 (s) 1.33 (s)	6.18 (d) J = 2.0 6.54 (d) J = 2.0	4.86 (d) $J_{H_A, H_{1a}}$ = 8.0	3.56 (ddd) J_{H_B, H_C} = 12.0 $J_{H_B, H_{3a}}$ = 4.5 $J_{H_B, H_{2e}}$ = 2.0	2.40 (dd) J_{H_C, H_B} = 12.0 $J_{H_C, H_{3a}}$ = 10.0	2 Me:0.90 (d), 1.04 (d) J = each 6.0 4 H:1.40—2.00 (m)
d-2[a]	Me	H	H	H	H	Me	*b*	*b*	4.92 (d) $J_{H_A, H_{1e}}$ = 3.0	*b*	*b*	*b*
d-3[a]	H	Me	H	H	Me	H	*b*	*b*	4.52 (d) $J_{H_A, H_{1a}}$ = 8.0	*b*	*b*	*b*

[a] Not isolated. [b] Could not be determined because of the overlapping with signals of the major products.

Table 4. ^{1}H N.m.r. chemical shifts (δ p.p.m.) and coupling constants (*J* in Hz) for compounds (**6**)—(**8**)

Compd.	Bu^t	4aH	Aromatic H	Others
(**6a**)	1.27 (s) 1.32(s)	5.76 (dd) *J* = 9.5, 3.0	6.42 (d) *J* = 2.0 6.56 (d) *J* = 2.0	1-H:6.20 (br s) 2-Me:1.63 (br s) 3,4-H:1.76—2.44 (4 H, m)
(**6b**)	1.27 (s) 1.33 (s)	5.50 (d) *J* = 9.0	6.31 (d) *J* = 2.0 6.56 (d) *J* = 2.0	1-H:6.21 (br s) 4-Me:1.00 (d) *J* = 6.0 2-Me:1.62 (br s) 3,4-H:1.80—2.45 (3 H, m)
(**7**)	1.26 (s) 1.31 (s)	5.56 (br s)	6.44 (d) *J* = 2.0 6.54 (d) *J* = 2.0	3-H:5.64 (m) 4-Me:1.78 (br s) 1,2-H:1.82—2.28 (2 H, m), 3.04—3.26 (2 H, m)
(**8**)	1.30 (s) 1.38 (s)	4.70 (d) *J* = 8.0	6.32 (d) *J* = 2.5 6.60 (d) *J* = 2.5	3-H:5.12—5.22 (m) 4-Me:1.16 (d) *J* = 6.0 2-Me:1.75 (br s) 4-H:2.40—2.72 (m) 1-H:3.40—3.48 (1 H, m), 3.56—3.88 (1 H, m)



Scheme 5.

which were further reduced to piperidinophenol (**4**). In contrast, $NaBH_4$ reduction gave the phenol (**3**) and/or cyclized products (**7**) and (**8**) depending upon the substituents on (**1**) and (**2**).

CAUTION. Although (**5**) was handled with extreme care, we experienced numbness of the mouth during the above experiment.

Experimental

M.p.s were determined on a Yanagimoto micro melting-point apparatus. I.r. spectra were measured as KBr pellets or liquid film on NaCl plates on a JASCO A-102 spectrophotometer. ^{13}C and ^{1}H N.m.r. spectra were determined at 100 MHz on a JEOL FX-100 spectrometer in $CDCl_3$ with Me_4Si as an internal standard and ^{1}H n.m.r. spectra of the products are summarized in Tables 3 and 4. Mass spectra were obtained on a JEOL JMS-01SG-2 spectrometer at 75 eV by using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Pyridinium halides (**1**) and the zwitterions (**2**) were prepared by the reported method.[2]

Reduction of Pyridinium Halides (**1**) *with Raney* Ni–Al *Alloy*.—In a typical procedure, Raney Ni–Al alloy (1.00 g) was gradually added to a mixture of compound (**1**) (1.00 g) in methanol (20 ml) and 30% aqueous potassium hydroxide (5 ml) and the mixture was refluxed for 10 min. It was then filtered and the filtrate evaporated under reduced pressure to leave a residue which was extracted with hot hexane (100 ml). The extract was evaporated under reduced pressure and the resultant residue was chromatographed using hexane–benzene (4:1) as eluant, to give (**5**) and (**6**).

6,8-*Di-t-butyl*-1,2,3,4-*tetrahydropyrido*[2,1-b]*benzoxazole* (**5a**). Colourless needles, m.p. 107—110 °C (decomp.) from aqueous methanol; $\nu_{max.}$(KBr) 1 600 cm^{-1} (C=C); δ_C 22.11 (t), 23.82 (t), 29.60 (q), 31.74 (q), 33.93 (s), 34.66 (s), 44.04 (t), 96.61 (d), 101.48 (d), 112.87 (d), 130.84 (s), 138.76 (s), 143.94 (s), and 145.28 (s); *m/z* 287 (M^+) (Found: C, 79.15; H, 10.25; N, 4.75. $C_{19}H_{29}NO$ requires C, 79.39; H, 10.71; N, 4.87%).

3-*eq-Methyl*-6,8-*di-t-butyl*-1,2,3,4-*tetrahydropyrido*[2,1-b]-*benzoxazole* (**5b**-1). Colourless needles, m.p. 190 °C (decomp.) from aqueous methanol; $\nu_{max.}$(KBr) 1 600 cm^{-1} (C=C); δ_C 18.64 (d), 29.60 (q), 30.88 (t), 31.74 (q), 33.93 (t), 34.66 (s), 50.80 (t), 96.36 (d), 101.05 (d), 112.57 (d), 130.78 (s), 138.45 (s), 143.94 (s), and 145.34 (s); *m/z* 301 (M^+) (Found: C, 79.95; H, 10.4; N, 4.6. $C_{20}H_{31}NO$ requires C, 79.68; H, 10.37; N, 4.65%).

4-*eq-Methyl*-6,8-*di-t-butyl*-1,2,3,4-*tetrahydropyrido*[2,1-b]-*benzoxazole* (**5b**-2_1). Colourless prisms, m.p. 154 °C (decomp.) from methanol; $\nu_{max.}$(KBr) 1 600 cm^{-1}; δ_C 16.85 (d), 24.02 (t), 29.69 (q), 31.10 (t), 31.84 (q), 34.03 (s), 35.00 (s), 43.80 (t), 101.41 (d), 102.10 (d), 112.89 (d), 131.00 (s), 138.91 (s), and 144.19 (s); *m/z* 301 (M^+) (Found: C, 79.65; H, 10.4; N, 4.65. $C_{20}H_{31}NO$ requires C, 79.68; H, 10.37; N, 4.65%).

3-*eq-Methyl*-6,8-*di-t-butyl*-1,2,3,4-*tetrahydropyrido*[2,1-b]-*benzoxazole* (**5c**). Colourless needles, m.p. 64—66 °C from aqueous methanol; $\nu_{max.}$(KBr) 1 600 cm^{-1} (C=C); δ_C 22.03 (d), 29.29 (q), 26.68 (q), 31.77 (q), 32.21 (t), 33.92 (s), 34.70 (s), 38.01 (t), 42.98 (t), 96.14 (d), 101.31 (d), 112.67 (d), 130.84 (s), 138.34 (s), 143.95 (s), and 145.36 (s); *m/z* 301 (M^+) (Found: C, 79.5; H, 10.5; N, 4.6. $C_{20}H_{31}NO$ requires C, 79.68; H, 10.37; N, 4.65%).

2-*eq*,4-*eq-Dimethyl*-6,8-*di-t-butyl*-1,2,3,4-*tetrahydropyrido*-[2,1-b]*benzoxazole* (**5d**-1). Colourless needles, m.p. 149—150 °C from methanol; $\nu_{max.}$(KBr) 1 600 cm^{-1}; δ_C 18.64 (d), 29.60 (q), 30.88 (t), 31.74 (q), 33.93 (s), 34.66 (s), 50.80 (t), 96.36 (d), 101.05 (d), 112.57 (d), 130.78 (s), 138.45 (s), 143.94 (s), and 145.34 (s); *m/z* 315 (M^+) (Found: C, 80.2; H, 10.55; N, 4.45. $C_{21}H_{33}NO$ requires C, 79.95; H, 10.54; N, 4.44%).

2-*Methyl*-6,8-*di-t-butyl*-3,4-*dihydropyrido*[2,1-b]*benzoxazole* (**6a**). Colourless prisms, m.p. 103—105 °C from aqueous methanol; $\nu_{max.}$(KBr) 1 595 and 1 660 cm^{-1} (C=C); mass *m/z* 299 (M^+) (Found: C, 80.4; H, 9.8; N, 4.65. $C_{20}H_{29}NO$ requires C, 80.22; H, 9.76; N, 4.68%).

2-*eq*,4-*eq-Dimethyl*-6,8-*di-t-butyl*-3,4-*dihydropyrido*[2,1-b]-*benzoxazole* (**6b**). Colourless viscous oil; $\nu_{max.}$(NaCl) 1 595 and 1 665 cm^{-1} (C=C) (Found: M^+, *m/z* 313.2405. $C_{21}H_{31}NO$ requires 313.2405).

Hydrogenation of Compounds (**5**) *and* (**6**) *with Raney* Ni (W_2) *Catalyst*.—In a typical procedure, a mixture of (**5**) or (**6**) (1.00 g) in methanol (100 ml) and a suspension of the catalyst in methanol (5 ml) was magnetically stirred under an atmosphere of hydrogen at room temperature for the time indicated in Table 2. The mixture was filtered and the filtrate treated as described above to give (**4**)[2] or (**5**).

Hydrogenation of Compounds (**1**) *and* (**2**) *with Raney* Ni (W_2) *Catalyst*.—In a typical procedure, a mixture of (**1**) or (**2**) (1.00 g) in methanol (50 ml) and a suspension of the catalyst in methanol (5 ml) was treated as described above to give (**4**) and/or (**5**).

$NaBH_4$ *Reduction of Compounds* (**1b**) *and* (**1d**).—The reduction was carried out in the previously reported manner.[4]

4-*Methyl*-6,8-*di-t-butyl*-3,2-*dihydropyrido*[2,1-b]*benzoxazole* (**7**). Colourless viscous oil; $\nu_{max.}$(KBr) 1 600 and 1 620 cm^{-1} (C=C); *m/z* 299 (M^+) (Found: C, 80.5; H, 10.0; N, 4.85. $C_{20}H_{29}NO$ requires C, 80.22; H, 9.76; N, 4.68%).

2-*eq*,4-*eq-Dimethyl*-6,8-*di-t-butyl*-1,4-*dihydropyrido*[2,1-b]-*benzoxazole* (**8**). Colourless needles, m.p. 100—102 °C (decomp.) from methanol; $\nu_{max.}$(KBr) 1 600 and 1 618 cm^{-1} (C=C); *m/z* 313 (M^+) (Found: C, 80.4; H, 10.05; N, 4.45. $C_{21}H_{31}NO$ requires C, 80.46; H, 9.96; N, 4.47%).

Hydrogenation of Compound (**7**) *and the* $NaBH_4$ *Reduction Product of* (**1d**) *with Raney* Ni (W_2) *Catalyst*.—A mixture of the

substrate (1.00 g) in methanol (100 ml) and a suspension of the catalyst in methanol (5 ml) was treated at room temperature for 1 h and worked up as described above to afford (**5b**) or (**5d**).

References

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