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Tandem [4+2]/[3+2] Cycloadditions of Nitroalkenes. 13. Synthesis of (-)-Platynecine

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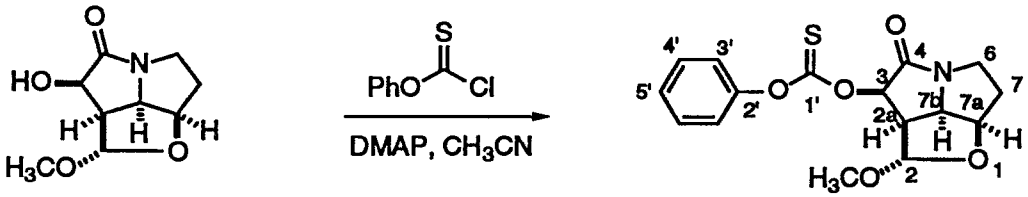
Supporting Information

(2*S*,2a*R*,3*R*,7a*R*,7b*R*)-Hexahydro-2-methoxy-3-[(phenoxythiocarbonyl)-oxy]-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (+)-8.



(+)-7 (+)-8

Analytical data for (+)-8

M.W. 335.38

mp: 140-141° C (Hexane/EtOAc)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.45-7.40 (m, 2 H, HC(4')), 7.32-7.29 (m, 1 H, HC(5')), 7.17-7.14 (m, 2 H, HC(3')), 6.28 (d, J = 8.3, 1 H, HC(3)), 5.12 (s, 1 H, HC(2)), 4.68 (dd, J = 3.7, 3.7, 1 H, HC(7a)), 4.22 (dd, J = 5.6, 3.2, 1 H, HC(7b)), 4.04 (ddd, J = 13.8, 9.0, 6.8, 1 H, $H_aC(6)$), 3.44 (dd, J = 8.3, 5.6, 1 H, HC(2a)), 3.34 (s, 3 H, $H_3C(8)$), 3.12 (ddd, J = 15.4, 10.9, 4.5, 1 H, $H_bC(6)$), 2.29-2.13 (m, 2 H, $H_2C(7)$.

^{13}C NMR: (100.6 MHz, $CDCl_3$)

194.10 (C(1')), 170.52 (C(4)), 153.43 (C(2')), 129.56 (C(4')), 126.73 (C(5'), 121.67 (C(3')), 105.77 (C(2)), 81.67 (C(3)), 79.73 (C(7a)), 66.30 (C(7b)), 54.90 (C(8)), 49.62 (C(2a)), 42.99 (C(6)), 29.59 (C(7)).

IR: (CCl_4)

2957 (m), 2928 (m), 2873 (w), 2858 (w), 1737 (s), 1491 (m), 1392 (w), 1336 (w), 1300 (m), 1282 (s), 1258 (m), 1245 (m), 1218 (s), 1209 (s), 1199 (s), 1118 (m), 1104 (m), 1080 (m), 1037 (w), 1024 (w), 1013 (m).

MS: (FAB)

336 (M^+1, 93), 306 (35), 305 (56), 304 (89), 183 (56), 182 (30), 155 (32), 152 (41), 135 (48), 122 (100), 121 (31), 119 (69), 103 (58).

TLC: R_f 0.33 (EtOAc/hexane , 2/1), [$KMnO_4$]

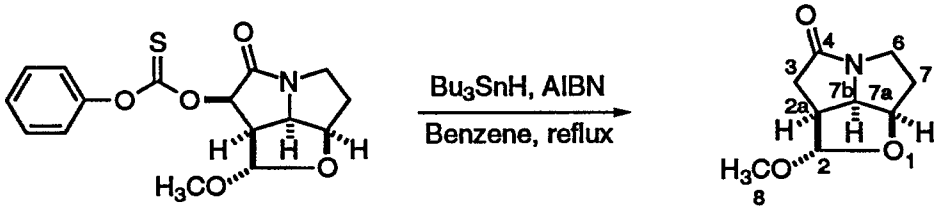
Rotation: $[\alpha]_D^{23}$ = +47.3 (c = 0.90, $CHCl_3$)

HPLC: Column: Regis, (*R*,*R*)-Whelko-01 (hexane/EtOAc, 70/30), 0.5 mL/min) t_R (+)-**8** 19.0 min (98.6%); t_R (-)-**8** 23.1 min (1.4%); 97% ee.

Analysis: ($C_{16}H_{17}NO_5S$)

Calcd:	C, 57.30;	H, 5.11;	N, 4.18;	S, 9.56.
Found:	C, 57.23;	H, 5.04;	N, 4.25;	S, 9.31.

(2*S*,2a*S*,7a*R*,7b*R*)-Hexahydro-2-methoxy-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (+)-(9).



(+)-**8** (+)-**9**

Analytical data for (+)-**9**

M.W. 183.21

mp: 94 -95° C (hexane/EtOAc)

^{1}H NMR: (400 MHz, $CDCl_3$)

4.74 (s, 1 H, HC(2)), 4.53 (dd, *J* = 4.6, 3.4, 1 H, HC(7a)), 4.29 (dd, *J* = 4.7, 3.4, 1 H, HC(7b)), 3.99-3.92 (m, 1 H, $H_aC(6)$, 3.28 (s, 3 H,$H_3C(8)$),

3.04 - 2.97 (m, 1H, $H_bC(6)$), 2.92 (dd, J = 9.3, 7.8, $H_aC(3)$), 2.82 (dd, J = 9.5, 6.2, 1 H, HC(2a)), 2.36 (d, J = 16.8, 1 H, $H_bC(3)$), 2.24-2.12 (m, 2 H, $H_2C(7)$).

^{13}C NMR: (100.6 MHz, $CDCl_3$)

177.28 (C(4)), 112.71 (C(2)), 81.20 (C(7a)), 70.19 (C(7b)), 54.36 (C(8)), 44.14 (C(2a)), 43.13 (C(6)), 37.57 (C(3)), 31.53 (C(7)).

IR: ($CHCl_3$)

3028 (w), 3023(w), 3018 (m), 3013 (m), 3010 (m), 2957 (m), 2937 (w), 2914 (w), 1691 (s), 1400 (w), 1338 (w), 1289 (w), 1251 (w), 1234 (m), 1194 (m), 1104 (m), 1090 (m), 1061 (s), 1000 (s).

MS: (FAB)

184 (M^++H, 100), 152 (8), 119 (15).

TLC: R_f 0.16 (EtOAc), [Anisaldehyde]

Rotation: $[\alpha]_D^{22}$ = +146.3 (c = 0.93, $CHCl_3$)

Analysis: ($C_9H_{13}NO_3$)

Calcd: C, 59.00 ; H, 7.15; N, 7.65.

Found: C, 58.86; H, 7.13; N, 7.66.

(2a*S*,7a*R*,7b*R*)-Hexahydro-2-hydroxy-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (10).

Analytical data for **10**

M.W. 169.18

^{1}H NMR: (500 MHz, CD_3OD)

5.37 (s, 1 H, HC(2)), 4.69 (dd, J = 4.9, 3.5, 1 H, HC(7a)), 4.43 (dd, J = 6.1, 3.4, 1 H, HC(7b)), 3.84 (ddd, J = 11.6, 9.2, 5.5, 1 H, $H_aC(6)$), 3.06-2.98 (m, 2 H, $H_bC(6)$, $H_aC(3)$), 2.82 (dd, J = 8.8, 6.2, 1 H, HC(2a)), 2.36 (d, J = 17.1, 1 H, $H_bC(3)$), 2.29-2.22 (m, 1 H, $H_aC(7)$) 2.11 (ddd, J = 14.4, 9.2, 5.1, 1 H, $H_bC(7)$).

^{13}C NMR: (125 MHz, CD_3OD)

180.12 (C(4)), 107.59 (C(2)), 82.16 (C(7a)), 72.10 (C(7b)), 46.39 (C(2a)), 43.85 (C(6)), 38.77 (C(3)), 32.18 (C(7)).

IR: ($CHCl_3$)

3040 (w), 3031 (m), 3025 (w), 1690 (s), 1411 (w), 1227 (m), 1219 (w), 1212 (w), 1200 (m).

MS: (FAB)

170 (M^++1, 78), 155 (60), 152 (23), 135 (40), 119 (100), 103 (47).

HRMS: (FAB) Cald for $C_8H_{12}NO_3$, 170.081718. Found, 170.081800

TLC: R_f 0.34 (10/1 $CHCl_3$, CH_3OH), [$KMnO_4$]

(-)-Platynecine (4).

10 (-)-platynecine

Analytical data for (-)-**4**

M.W. 157.2

mp: 145 -146° C (acetone)

^{1}H NMR: (500 MHz, CD_3OD)

4.23-4.22 (m, 1 H, HC(1)), 3.93 (d, J = 5.5, 2 H, $H_2C(8)$), 3.24 (dd, J = 8.0, 3.2, 1 H, HC(7a)), 3.21-3.17 (m, 1 H, $H_aC(3)$), 3.10-3.05 (m, 1 H, $H_aC(5)$), 2.86-2.80 (m, 1 H, $H_bC(3)$), 2.78-2.74 (m, 1 H, $H_bC(5)$) 2.47-2.39 (m, 1 H, HC(7)), 2.02-1.94 (m, 1 H, $H_aC(6)$), 1.90-1.82 (m, 2 H, $H_2C(2)$), 1.74-1.68 (m, 1H, $H_bC(6)$).

^{13}C NMR: (125 MHz, CD_3OD)

73.15 (C(1)), 72.62 (C(7a)), 61.73 (C(8)), 56.58 (C(5)), 54.81 (C(3)), 45.08 (C(7)), 37.33 (C(2)), 28.87 (C(6)).

IR: ($CHCl_3$)

3329 (br), 3026 (s),3021 (s), 3005 (s), 2972 (s), 2943 (s), 2882 (s), 1442 (w), 1351 (w), 1227 (m), 1216 (m), 1168 (w), 1124 (m), 1050 (w), 1011 (m).

MS: (FAB)

158 (M^++ 1, 100), 155 (30), 135 (20), 119 (52) 103 (24).

TLC: R_f 0.09 (10/5/1, $CHCl_3$, CH_3OH, NH_4OH), [$KMnO_4$]

Rotation: $[\alpha]_D^{22}$ = -61.5 (c = 1.0, $CHCl_3$)

Analysis: ($C_8H_{15}NO_2$)

Calcd:	C, 61.12 ;	H, 9.62;	N, 8.91.
Found:	C, 61.12 ;	H, 9,63;	N, 8.71.

(2a*S*,7a*R*,7b*R*)-Hexahydro-2-hydroxy-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (**10**)