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SYNTHETIC PHOTOCHEMISTRY. SYNTHESIS OF (±)OLIVEROLINE AND (±)USHINSUNINE

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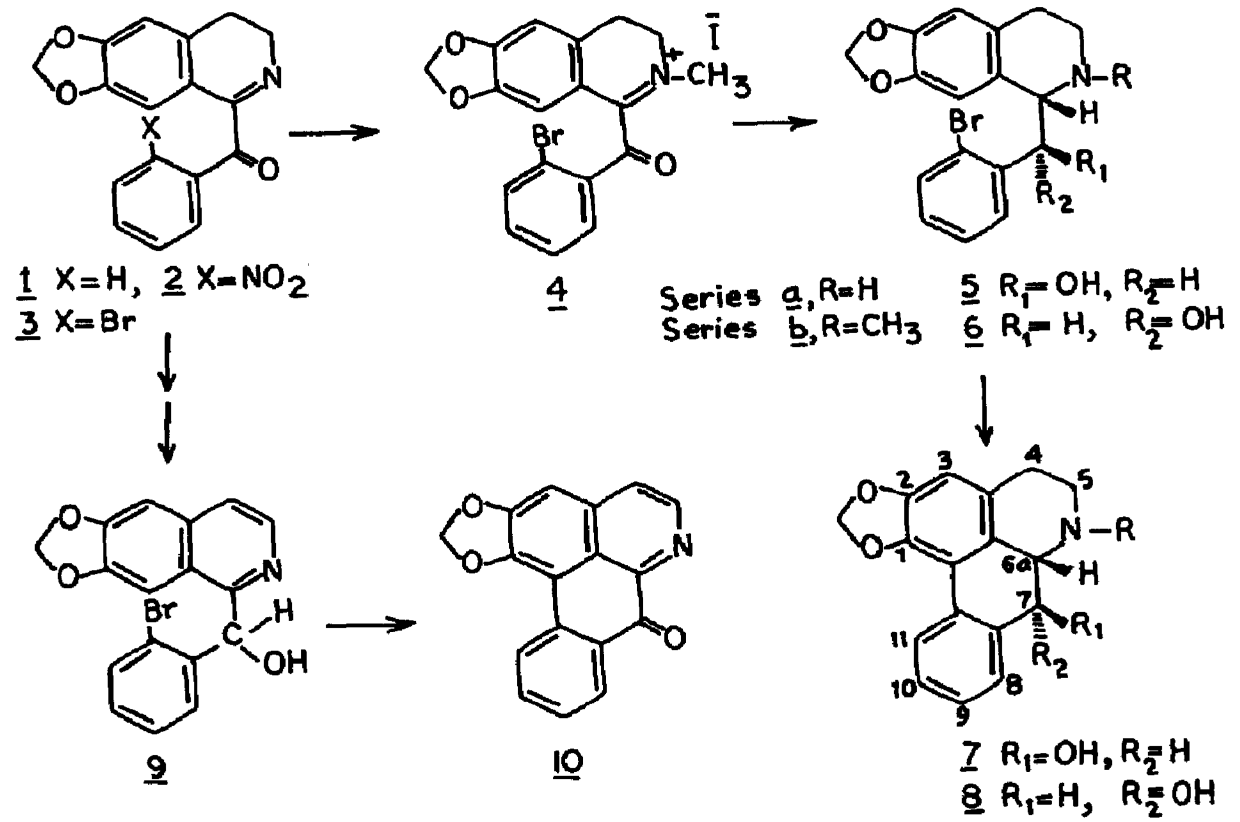
Summary : Sodium borohydride reduction of 1-(2'-Bromobenzoyl)-2-methyl-3,4-dihydro-6,7-methylenedioxyisoquinolinium iodide (4) gave a mixture of alcohols which on irradiation in dil.HCl afforded (±) oliveroline and (±)ushinsunine.

Synthesis of aporphine alkaloids having a 7-hydroxy group cis to the 6a hydrogen[1] (7) does not seem to have been reported, although Pschorr cyclisation route to the trans isomers (8) is known[2]. This may be due to the fact that reduction of the intermediate keto-imines like 1 and 2 gives products corresponding to trans stereochemistry almost exclusively[3,4]. We have found that sodium borohydride reduction of the quaternary compound 4 ($C_{18}H_{15}BrINO_3$; m.p.192°C) furnishes a mixture of alcohols containing[5] 40 % of the desired isomer 5b which can be photocyclised[6] with retention of the benzylic hydroxyl group[7]. For cyclisation the mixture of 5b and 6b (200 mg) was dissolved in 350 ml of 3 % HCl and irradiated (3 hr) with a 125W high pressure mercury lamp using a quartz filter. After work up, preparative chromatography afforded 7b (13 mg, 26 % yield based on 5b) ($C_{18}H_{17}NO_3$; m.p. 162-3°C). Its identity as (±) oliveroline was confirmed by spectroscopic data [(δ^{CDCl_3} 2.55 (s,3H,NMe), 3.47 (d,1H,J = 12 Hz, H_{6a}), 4.61 (d,1H,J=12Hz, H_7), 5.96 and 6.08 (2d, 2H, J = 1.8 Hz, O-CH_2-O, $H_{1,2}$), 6.60 (s,1H,H_3), 7.23 and 7.62 (m, 3H, $H_{8,9,10}$), 8.08 (m,1H,H_{11}); m/e 295 (M^+), 294 $(M-1)^+$, 277, 252, 190, 165, 130, 105, 91; $\lambda_{max}^{C_2H_5OH}$ (log ∈) 273 (3.92),315(3.42)] and t.l.c. comparison with a natural sample[8]. The chromatogram also furnished (±)ushinsunine[1] 8b (15.6 mg) [($C_{18}H_{17}NO_3$;m.p.144-5°C; δ^{CDCl_3} 2.55 (s,3H,NMe), 3.25(d,1H,J=2.5 Hz,H_{6a}), 4.82 (d, 1H, J = 2.5 Hz,H_7), 5.93 and 6.08 (2d, 2H, J = 1.5 Hz, -O-CH_2-O-, $H_{1,2}$), 6.58 (s,1H,H_3), 7.19 and 7.62 (m,3H,$H_{8,9,10}$), 8.21 (m,1H,H_{11}); m/e 295 (M^+), 294 $(M-1)^+$, 277, 252, 190, 165, 130, 105, 91; $\lambda_{max}^{C_2H_5OH}$ (log∈) 272 (3.98), 323 (3.48)] besides some starting material[9] (40 mg).

Sodium borohydride reduction of 3 gave a mixture of carbinols containing 15 % of 5a. Irradiation of this mixture furnished (±)norushinsunine[1] 8a [($C_{17}H_{15}NO_3$; 20 % yield; m.p. 202-3°C; m/e 281 (M^+), 280, 263, 262, 261, 253, 252, 251)] which was N-methylated[10] to 8b. Along with unreacted starting material, a small quantity of 7a [($C_{17}H_{15}NO_3$; m.p. 204-5°C; m/e 281 (M^+), 280, 263, 262, 261, 253, 252, 251] was also obtained. Attempted photocyclisation of the bromoketone 3 was unsuccessful. However, the alcohol 9 [$C_{17}H_{12}BrNO_3$; m.p. 171-3°C; m/e 359, 357 (M^+)] afforded the yellow alkaloid liriodenine[1] 10 [($C_{17}H_9NO_3$; m.p. 277°C; m/e 275(M^+); $\lambda_{max}^{C_2H_5OH}$ (log ∈) 247 (4.49), 268.5 (4.41), 310 (3.91), 413 (3.80)] in 37 % yield.



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8. We are very grateful to Prof. A.Cave for a sample of (-) oliveroline.
9. Reduction and photocyclisation of the iodo analogue of 4 gave essentially similar results.
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