

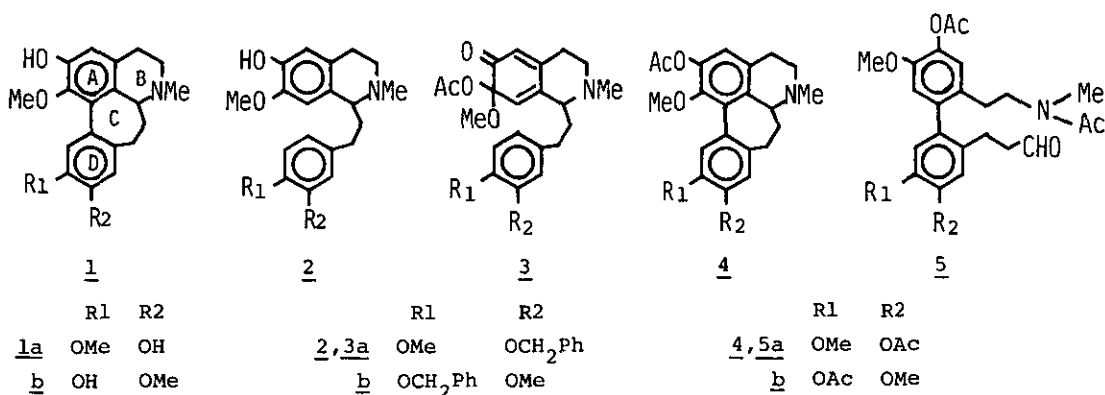
A SYNTHESIS OF (±)-2-HYDROXYHOMOAPORPHINES
BEARING A HYDROXYL GROUP ON THE D-RING

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Previously we have found that $\text{Pb}(\text{OAc})_4$ (LTA) oxidation of 1-phenethyl-6-tetrahydroisoquinolinols in CH_2Cl_2 gives o-quinol acetates(o-QAs), treatment of which with $\text{Ac}_2\text{O}\cdot\text{c}\cdot\text{H}_2\text{SO}_4$ leads to 2-acetoxymorphine¹⁾ together with biphenyl compounds. Now we wish to report a synthesis of (±)-2-hydroxyhomoaporphines(1) bearing a hydroxyl group on the D-ring by use of the method.

o-QA(3a) prepared by LTA oxidation of 2a was treated with $\text{Ac}_2\text{O}\cdot\text{c}\cdot\text{H}_2\text{SO}_4$ in CH_3CN to give 2,10-diacetoxymorphine(4a) (oil, 61.5%) [NMR δ : 6.84(1H, s, 3-H), 6.92(1H, s, 9-H), 7.10(1H, s, 12-H); MS: m/z 425(M^+)] accompanied with a biphenyl product (5a) (oil, 6 %) [MS: m/z 485(M^+)]. Hydrolysis of 4a with 10% HCl in boiling MeOH gave (±)-2,10-dihydroxyhomoaporphine (1a) (mp 189.5-193°, 77.3 %) [NMR δ : 6.58(1H, s, 3-H), 6.66(1H, s, 9-H), 6.90(1H, s, 12-H)]. Similarly, 3b gave 1b (mp 134.5-137°) [NMR δ : 6.40(1H, s, 3-H), 6.55(1H, s, 9-H), 7.13(1H, s, 12-H)] via 4b (oil) [NMR δ : 6.80(1H, s, 9-H), 6.84(1H, s, 3-H), 7.20(1H, s, 12-H); MS m/z 425(M^+)] in 54 % overall yield. Synthesis of the related compounds will be also discussed.



REFERENCE

- 1) O.Hoshino, H.Ogose, and B.Umezawa, 4th International Conference on Organic Synthesis, Tokyo, Aug. 22-27, 1982.