

A SYNTHESIS OF (±)-3-HYDROXYHOMOAPORPHINES

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In the course of our studies on photochemical reaction of a phenolic N-(β-phenethyl) phenylpropionamide, we found that the photocyclization gave useful key compounds(1) for synthesis of (±)-3-hydroxyhomoaporphines(2).

A methanolic solution of amide(3a) or (3b) in the presence of KOH under N₂ was irradiated at 0-5°C by a 200W high pressure mercury lamp for 1-2 hr to give a lactam(1a) (mp 265-267°C, 40.1%) [NMR(CDCl₃) δ: 6.33, 6.60 (each 1H, d, J=3.2Hz, Ar-H), 6.70, 6.80 (each 1H, s, Ar-H); MS: m/z 357 (M⁺)] or (1b) (mp 281-284°C, 43.5%) [NMR(CDCl₃) δ: 6.28, 6.56 (each 1H, d, J=3.2Hz, Ar-H), 6.67, 6.68 (each 1H, s, Ar-H); MS: m/z 341 (M⁺)] and a debrominated amide(4a) (32.8%) or (4b) (37.4%), respectively. Bischler-Napieralski reaction (POCl₃, CH₃CN, reflux) of 1a gave 6,6a-dehydrohomoaporphine(5a) (oil, 61.6%) [NMR(CDCl₃) δ: 6.60, 6.64, 6.72 (each 1H, s, Ar-H); MS: m/z 339 (M⁺)], reduction of which with NaBH₄ in MeOH afforded N-norhomoaporphine (6a) (oil, 86.8%) [NMR(CDCl₃) δ: 6.60, 6.62, 6.70 (each 1H, s, Ar-H)]. N-Methylation (CH₂O-MeOH; NaBH₄) of 6a gave 2a (oil) [NMR(CDCl₃) δ: 2.31 (3H, s, N-CH₃), 6.58, 6.60, 6.68 (each 1H, s, Ar-H)] in good yield. Attempts to synthesize some (±)-3-hydroxyhomoaporphines by the present method will be described.

