Supporting Information

Electrophilic Induced Cyclization Reaction of Hexahydroindolinone Derivatives and its Application Toward the Synthesis of (±)-Erysotramidine

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Supporting Information Available: Spectroscopic and experimental procedures for 7-bromo-1-(3,3-diethoxypropyl)-3a-methyl-1,3,3a,4,5,6-hexahydroindol-2-one and 1-(3,3-diethoxypropyl)-3a-methyl-7-vinyl-1,2,2a,4,5,6-hexahydroindol-2-one. ¹H and –¹³C-NMR spectra for new compounds lacking elemental analyses together with an ORTEP drawing for structure **35**. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

General Experimental Section Paragraph: Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70eV. Unless otherwise noted, all reactions were performed in flame dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate-hexane mixture as the eluent unless specified otherwise.

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Ortep Drawing of Compound 35

Supplemental Experimental Section

7-Bromo-1-(3,3-diethoxypropyl)-3a-methyl-1,3,3a,4,5,6-hexahydroindol-2-one. A solution of hexahydroindolone **25** (5.0 mmol) in CH_2Cl_2 (50 mL) was cooled in an ice bath. Bromine (0.25 mL, 5.0 mmol) was slowly added *via* a syringe and the colorless mixture was stirred for 5 min. Triethylamine (2.1 mL, 15.0 mmol) was then added in one portion. The mixture was allowed to warm to rt, stirred for 10 min, and washed with water (50 mL). The organic phase was separated, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using a 30% Et_2O /hexane mixture as the eluent. 7-Bromo-1-(3,3-diethoxy-propyl)-3a-methyl-1,3,3a,4,5,6-hexahydro-indol-2-one was obtained in 80% yield as a colorless oil; IR (neat) 1719, 1671, 1361, 1063, and 1024 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.13 (s, 3H); 1.17 (t, 3H, $J = 7.0$ Hz), 1.18 (t, 3H, $J = 7.0$ Hz), 1.50-1.62 (m, 1H), 1.70-2.01 (m, 5H), 2.18 (d, 1H, $J = 15.6$ Hz), 2.29 (d, 1H, $J = 15.6$ Hz), 2.54 (d, 1H, $J = 8.7$ Hz), 2.55 (d, 1H, $J = 8.7$ Hz), 3.43-3.54 (m, 2H), 3.59-3.70 (m, 2H), 3.84-4.02 (m, 2H), and 4.54 (t, 1H, $J = 6.0$ Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 15.5, 20.6, 25.6, 32.3, 33.6, 35.9, 37.6, 42.2, 46.3, 61.3, 61.6, 96.8, 101.2, 142.0, and 174.6.

1-(3,3-Diethoxypropyl)-3a-methyl-7-vinyl-1,3,3a,4,5,6-hexahydroindol-2-one. A mixture of the above bromo enamido lactam (0.2 g, 0.56 mmol), vinyl tributyltin (0.24 mL, 0.83 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.02 g, 0.028 mmol), and Bu_4NBr (0.21 g, 0.67 mmol) in DMF (2.0 mL) was heated at 100 $^\circ\text{C}$ for 5 h. The mixture was diluted with Et_2O and washed with water. The organic phase was dried over MgSO_4 , filtered, and concentrated. The crude product was purified by flash chromatography on silica gel using a 50% Et_2O /hexane mixture as the eluent. 1-(3,3-Diethoxy-propyl)-3a-methyl-7-vinyl-1,3,3a,4,5,6-hexahydro-indol-2-one was obtained in 60% yield as a colorless oil; IR (neat) 1718, 1640, 1332, 1131, and 1062 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.08 (s, 3H), 1.16 (t, 3H, $J = 7.1$ Hz), 1.17 (t, 3H, $J = 7.1$), 1.46 (td, 1H, $J = 13.3$ and 3.8 Hz),

1.64-1.83 (m, 4H), 2.00 (qt, 1H, J = 10.5 and 5.2 Hz), 2.12-2.20 (m, 1H), 2.16 (d, 1H, J = 15.7 Hz), 2.22 (d, 1H, J = 15.7 Hz), 2.32 (dd, 1H, J = 17.1 and 7.1 Hz), 3.41-3.48 (m, 2H), 3.52 (ddd, 1H, J = 14.8, 10.0, and 5.5 Hz), 3.58-3.66 (m, 2H), 4.03 (ddd, 1H, J = 16.2, 10.0, and 5.5 Hz), 4.50 (t, 1H, J = 5.7 Hz), 4.97 (dd, 1H, J = 11.0 and 1.0 Hz), 5.07 (dd, 1H, J = 17.1 and 1.0 Hz), and 6.76 (dd, 1H, J = 17.1 and 11.0 Hz); ^{13}C -NMR (100 MHz, CDCl_3) δ 15.5, 18.2, 24.8, 25.5, 31.7, 34.1, 39.6, 46.6, 61.8, 61.9, 101.3, 111.2, 112.2, 132.8, 142.9, and 175.4.