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AZIRIDINE IN ALKALOID SYNTHESIS. VI. ALTERNATIVE SYNTHETIC APPROACH TO THE BASIC SKELETON OF ERYTHRINA ALKALOIDS

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Abstract —— Treatment of the aziridine (2) with 3-bromocyclohex-2-en-1-one afforded the bromo derivative (4), which was then thermally cyclized to give the enaminone (8) siteselectively. Reaction of 10 with mercuric acetate furnished 12 instead of the desired erythrinan-type compound, whereas the acid-catalyzed cyclization of 8 yielded the desired cyclized product (14).

Aziridine and its quaternary derivatives have been shown to be useful intermediates as reactive species for the synthesis of various types of naturally occurring alkaloids.[1-4] We have already succeeded in the syntheses of several isoquinoline alkaloids, such as sendaverine,[5] cherylline,[6] γ-lycorane[7] and reframidine,[8] utilizing aziridine derivatives as key intermediates. It was therefore of interest to examine the application of the above synthetic strategy for the preparation of the other type of isoquinoline alkaloids.

Thus, we have investigated the synthesis of the basic skeleton of erythrinan alkaloid and here wish to report an alternative synthetic approach.

Reaction of ethyleneimine with 3,4-dimethoxyphenethyl bromide (1) gave the aziridine derivative (2), which was then treated with 3-bromocyclohex-2-en-1-one (3) to afford the bromo-enaminone (4) together with the dimer (5). Intramolecular γ-alkylation[9] of 4 with LDA furnished the enaminone (6), which was already converted[10] into hexahydroapoerysopine dimethyl ether (7) arising from the acid-catalyzed apo-rearrangement of tetrahydroerythraline. In order to synthesize an erythrinan skeleton, an intramolecular α-alkylation of 4 was investigated. Although Iida[11] reported the silver-catalyzed α-alkylation for the enaminone system and obtained the desired product in low yield, the thermal cyclization of 4

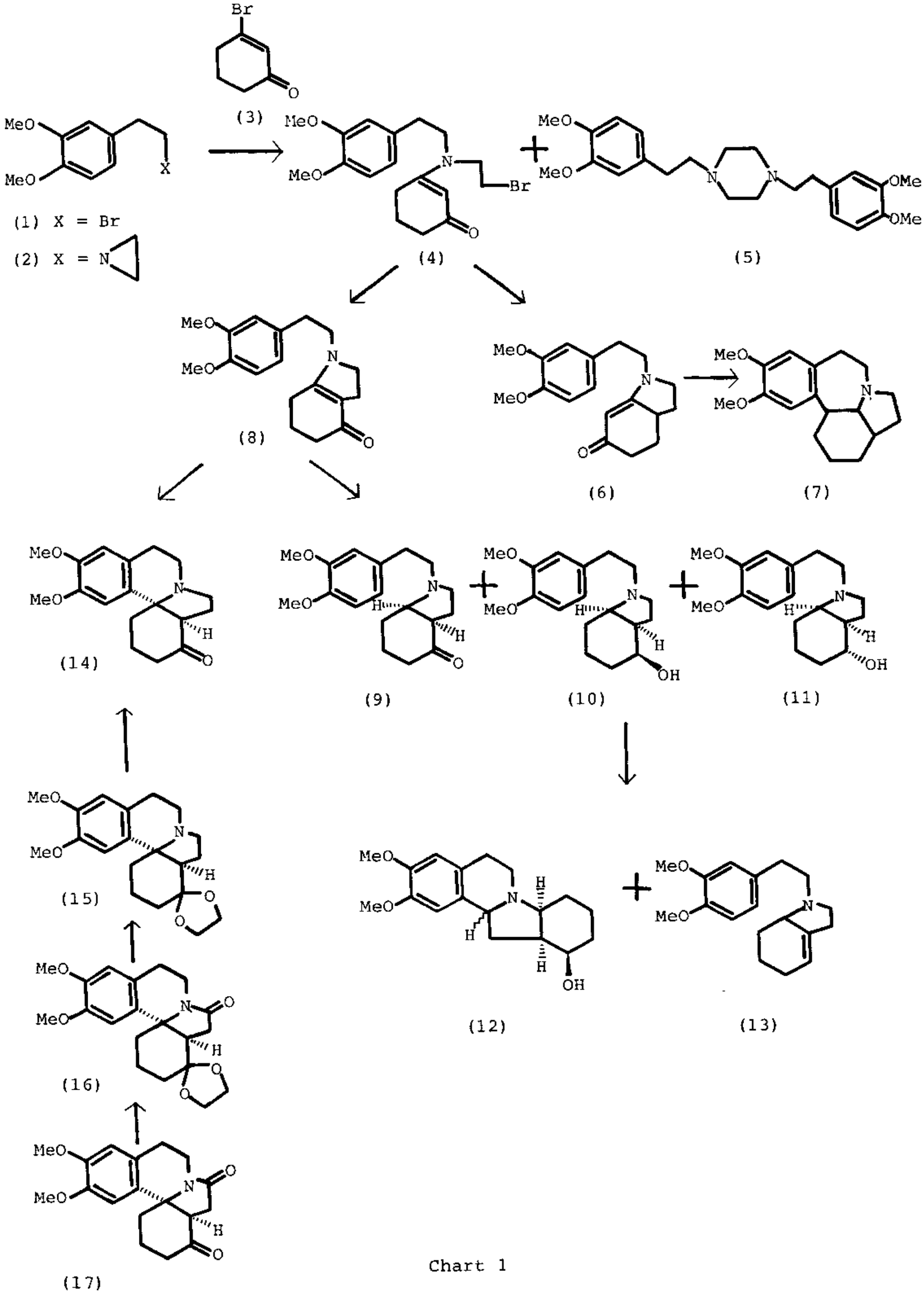

Chart 1

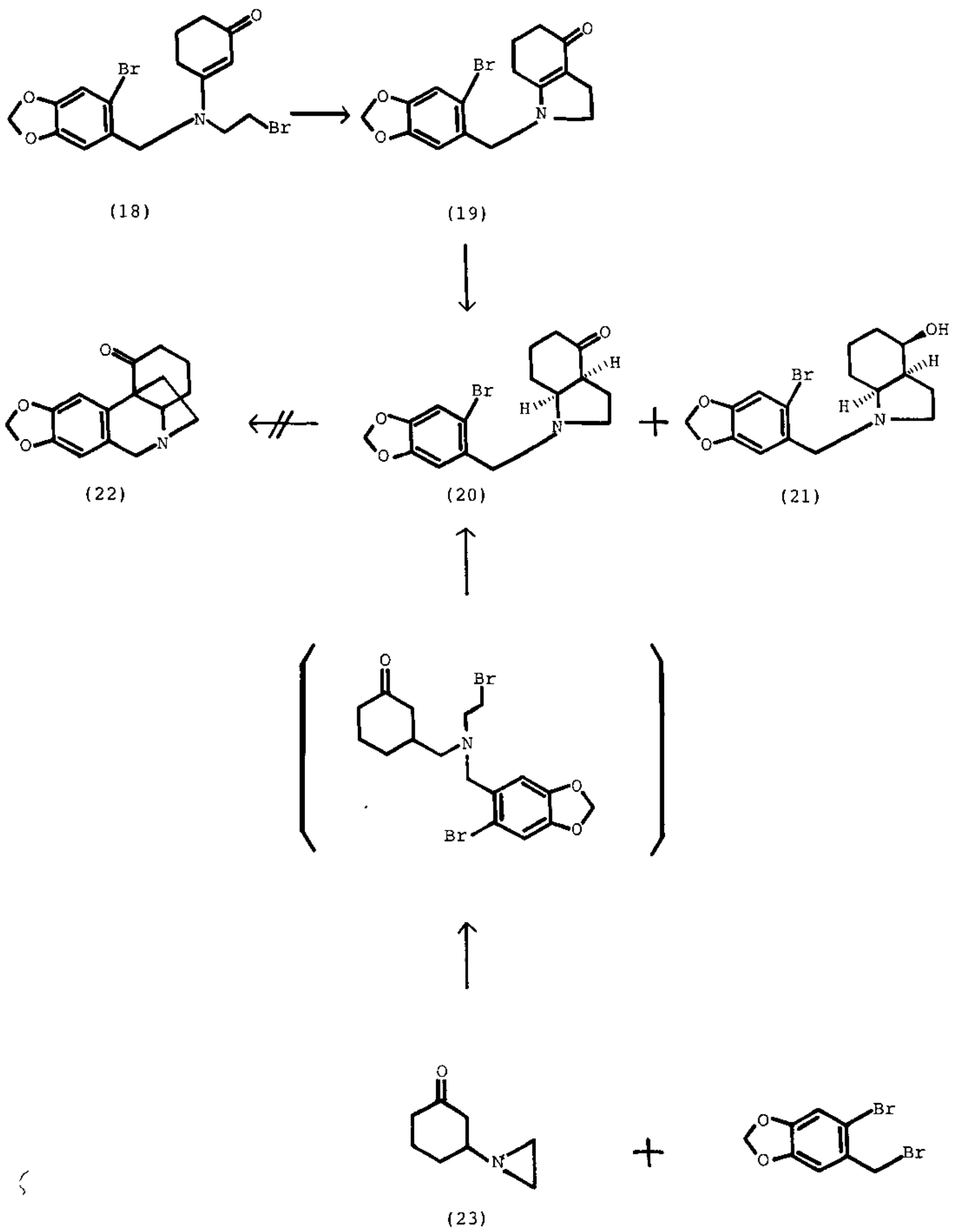

Chart 2

in the presence of sodium iodide brought about the α-cyclization siteselectively to give rise to the enaminone (8) in satisfactory yield. Reduction of 8 with $LiAlH_4$ afforded the alcohol (10) in 73.4 % yield, together with the ketone (9) and the cis-alcohol (11) in 2 % and 14.8 % yields, respectively. Attempted cyclization of 10 into the erythrinan skeleton by treatment with mercuric acetate afforded the isoquinoline derivative (12) together with the dehydrated compound (13). Although difficulties were encountered in the above conversion under the various reaction conditions, the acid-promoted cyclization of 8 gave the desired compound (14), whose stereochemistry was determined to be B/C-cis by comparison with the authentic sample prepared from the known compound (15)[12] by successive ketalization, reduction and deketalization (Chart 1).

We next investigated the preparation of crinane-type alkaloid utilizing the above synthetic approach. The dibromo-enaminone (18)[7] was converted into the enaminone (19)[11] as described above in good yield. Reduction of 19 with $LiAlH_4$ yielded the ketone (20) and the alcohol (21) in 16.8 % and 35.3 % yields, respectively. The former compound was also obtained from the aziridine derivative (23)[13] by treatment with 2-bromo-3,4-methylenedioxybenzyl bromide and subsequently potassium tert-butoxide in 72.8 % over-all yield. However, the cyclization of 20 into 22 under the various reaction conditions, e.g., benzyne reaction or photocyclization, resulted in failure.

Thus, we could achieve the formation of the basic skeleton of erythrinan-type alkaloids, although the yield was not satisfactory for its conversion into naturally occurring alkaloids (Chart 2).

EXPERIMENTAL SECTION

Melting points are not corrected. IR spectra were measured with a Hitachi 260-10 spectrophotometer, NMR spectra with a JEOL JNM-FX 100 spectrometer using tetramethylsilane as an internal reference. Mass spectra were taken with a JEOL JMS-D 300 spectrometer.

N-(3,4-Dimethoxyphenethyl)aziridine (2) To a stirred solution of ethyleneimine (20 ml) in dry benzene (20 ml) in the presence of potassium carbonate (5 g) was added a solution of 3,4-dimethoxyphenethyl bromide (4.9 g) in benzene (30 ml) at ambient temperature over the period of 0.5 h. After stirring for 12 h, the solvent and an excess of reagent were distilled off to give the residue which was treated with water and extracted with benzene. The benzene layer was washed with water and dried (Na_2SO_4). Evaporation of the solvent afforded the residure which was chromatographed on neutral alumina. Elution with methylene chloride gave the aziridine (2) (3.59 g, 86.7 %) as an oil. NMR δ ($CDCl_3$) 1.07 (2H, m, aziridine protons), 1.73 (2H, m, aziridine protons), 2.42 (2H, br t J = 7.1 Hz, $ArC\underline{H}_2CH_2N$), 2.76 (2H, br t, J = 7.1 Hz, $ArCH_2C\underline{H}_2N$), 3.85 (3H, s, OMe), 3.86 (3H, s, OMe), 6.75 - 6.77 (3H, m, ArH); m/z 207 ($\underline{M}^+$). High MS m/z 207.1257. $C_{12}H_{17}NO_2$ requires 207.1257.

<u>3-(N-β-Bromoethyl-N - 3,4-dimethoxyphenethyl)aminocyclohex-2-en-1-one (4) and The Dimer (5)</u> A solution of the aziridine (2) (4.14 g) and 3-bromocyclohex-2-en-1-one (3) (3.5 g) in acetone (100 ml) was heated under reflux for 50 h. After evaporation of the solvent, the residue was chromatographed on neutral alumina. Elution with methylene chloride afforded the dimer (5) (1.82 g, 44 %) as needles, mp 119 - 120 °C (from n-hexane-acetone). Anal. calcd for $C_{24}H_{34}N_2O_4$: C, 69.53; H, 8.27; N, 6.76. Found: C, 69.67; H, 8.39; N, 6.50 %. NMR δ ($CDCl_3$) 2.59 - 2.79 (16H, m, 8 x CH_2), 3.85 (6H, s, 2 x OMe), 3.87 (6H, s, 2 x OMe), 6.75 - 6.76 (6H, m, ArH); m/z 414 ($\underline{M}^+$). Further elution with methylene chloride furnished the enaminone (4) (4.18 g, 54.7 %) as prisms, mp 106 - 107 °C (from n-hexane). Anal. calcd for $C_{18}H_{24}BrNO_3$: C, 56.55; H, 6.33; N, 3.66. Found: C, 56.92; H, 6.45; N, 3.52 %. IR νmax ($CHCl_3$) 1600, 1550 cm^{-1}; NMR δ ($CDCl_3$) 1.85 - 2.05 (2H, m, CH_2), 2.21 - 2.43 (4H, m, 2 x CH_2), 2.81 (2H, t, J = 7.2 Hz, CH_2), 3.39 - 3.61 (6H, m, 3 x CH_2), 3.86 (3H, s, OMe), 3.87 (3H, s, OMe), 5.24 (1H, s, olefinic proton), 6.64 - 6.87 (3H, m, ArH); m/z 381 ($\underline{M}^+$); High MS m/z 381 ($\underline{M}^+$); High MS m/z 381.0927. $C_{18}H_{24}BrNO_3$ requires 381.0938.

<u>γ-Alkylation of 4</u> To a stirred solution of LDA (prepared from 7 ml of 15 % hexane solution of n-butyllithium and 1.73 ml of diisopropylamine) in dry tetrahydrofuran (30 ml) was added a solution of 4 (3.82 g) in tetrahydrofuran (30 ml) at -78 °C over the period of 3 h, and the resulting mixture was further stirred for 2 days at room temperature. The reaction was quenched by addition of water (30 ml) and the mixture was extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated to give the residue which was chromatographed on neutral alumina. Elution with methylene chloride yielded the

enaminone (6) (0.95 g, 31.6 %) as prisms, mp 91 - 92° C (from *n*-hexane-benzene) (lit.,[10] mp 45° C); NMR δ ($CDCl_3$) 1.41 - 1.88 (2H, m, CH_2), 2.02 - 2.44 (4H, m, 2 x CH_2), 2.80 (2H, t, J = 7.2 Hz, $ArCH_2$), 2.81 (1H, m, CH), 3.19 - 3.51 (4H, m, 2 x CH_2), 3.87 (6H, s, 2 x OMe), 5.10 (1H, s, olefinic proton), 6.66 - 6.78 (3H, m, ArH); m/z 301 (*M*$^+$); High MS m/z 301.1673. $C_{18}H_{23}NO_3$ requires 301.1676.

α-Alkylation of 4 A solution of 4 (3.82 g) and sodium iodide (9 g) in dimethylformamide (15 ml) and toluene (50 ml) was heated under reflux for 7 h. After evaporation of the solvent, the residue was treated with 10 % sodium carbonate solution and extracted with benzene. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated to the residue, which was chromatographed on neutral alumina. Elution with methylene chloride gave the enaminone (8) (2.47 g, 82.1 %) as a gum. IR νmax ($CHCl_3$) 1590, 1550 cm^{-1}; NMR δ ($CDCl_3$) 1.71 - 2.01 (4H, m, 2 x CH_2), 2.15 - 2.26 (2H, m, CH_2), 2.70 - 2.88 (4H, m, 2 x CH_2), 3.40 (2H, t, J = 6.7 Hz, NCH_2), 3.61 (2H, t, J = 10 Hz, NCH_2), 3.85 (3H, s, OMe), 3.86 (3H, s, OMe), 6.62 - 6.86 (3H, m, ArH); m/z 301 (*M*$^+$); High MS m/z 301.1690. $C_{18}H_{23}NO_3$ requires 301.1676.

Reduction of 8 with Lithium Aluminum Hydride To a stirred suspension of $LiAlH_4$ (1.52 g) in tetrahydrofuran (40 ml) was added a solution of the enaminone (8) (6 g) in tetrahydrofuran (50 ml) and the resulting mixture was heated under reflux for 3 h. After addition of water, the insoluble material was filtered off and the filtrate was dried (Na_2SO_4), and concentrated to the residue, which was chromatographed on neutral alumina. Elution with methylene chloride afforded the ketone (9) (0.12 g, 1.99 %) as an oil. IR νmax ($CHCl_3$) 1720 cm ; NMR δ ($CDCl_3$) 1.57 - 2.01 (6H, m, 3 x CH_2), 2.10 - 2.50 (4H, m, 2 x CH_2), 2.50 - 2.95 (5H, m, 2 x CH_2 and CH), 3.05 - 3.34 (1H, m, NCH), 3.85 (3H, s, OMe), 3.86 (3H, s, OMe), 6.64- 6.82 (3H, m, ArH); m/z 303 (*M*$^+$); High MS m/z 303.1812. $C_{18}H_{25}NO_3$ requires 303.1833. The *trans*-alcohol (10) (4.46 g, 73.4 %) was obtained from the second eluant as an oil. IR νmax ($CHCl_3$) 3350, 1590 cm^{-1}; NMR δ (CDCl) 1.15 - 3.45 (16H, m, 7 x CH_2 and 2 x CH), 3.55 - 3.70 (1H, m, C*H*OH), 3.85 (3H, s, OMe), 3.88 (3H, s, OMe), 4.62 (1H, br s, OH), 6.67 - 6.86 (3H, m, ArH); m/z 305 (*M*$^+$); High MS m/z 305.1984. $C_{18}H_{27}NO_3$ requires 305.1989. Further elution with methylene chloride gave the *cis*-alcohol (11) (0.9 g, 14.8 %) as needles, mp 78 - 79°C (from *n* hexane-ether). *Anal*. calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59. Found:

C, 70.92; H, 9.11 N; 4.52 %. IR νmax ($CHCl_3$) 3450, 1590 cm^{-1}; NMR δ ($CDCl_3$) 1.15 3.09 (15H, m, 7 x CH_2 and CH), 3.15 - 3.40 (1H, m, NCH), 3.41 - 3.70 (1H, m, C*H*OH), 3.85 (3H, s, OMe), 3.87 (3H, s, OMe), 6.68 - 6.85 (3H, m, ArH); m/z 305 (*M^+*).

Cyclization of 10 with Mercuric Acetate A mixture of 10 (1 g), mercuric (II) acetate and 5 % acetic acid (50 ml) was heated under reflux for 1 h, and then H_2S gas was bubbled into the above solution at the same temperature for 1 h. After an insoluble material had been filtered off, the filtrate was concentrated to the half of volume and diluted with 50 % ethanol (100 ml). The mixture was adjusted to pH 6 by addition of sodium bicarbonate, and then an excess of sodium borohydride was added to the above mixture. The resulting solution was stirred for 12 h at room temperature. After evaporation of the solvent, the residue was chromatographed on neutral alumina. Elution with methylene chloride furnished the dehydrated product (13) (0.55 g, 51.8 %) as an oil. NMR δ ($CDCl_3$) 1.17 - 3.37 (15 H, m, 7 x CH_2 and CH), 3.86 (3H, s, OMe), 3.88 (3H, s, OMe), 5.43 (1H, m, olefinic proton), 6.75 - 6.78 (3H, m, ArH); High MS m/z 287.1895. $C_{18}H_{15}NO_2$ requires 287.1885. The hydrochloride of 13, mp 214 - 215 °C, crystallized from *n*-hexane-methylene chloride. *Anal*. calcd for $C_{18}H_{26}NO_2Cl$: C, 66.76; H, 8.09; N, 4.32. Found: C, 66.31; H, 8.15; N, 4.32 %. Further elution with methylene chloride afforded the cyclized product (12) (0.08 g, 8.05 %) as prisms, mp 126 - 127 °C (from *n*-hexane-methylene chloride). *Anal*. calcd for $C_{18}H_{25}NO_3$: C, 71.25; H, 8.31; N, 4.62. Found: C, 70.80; H, 8.36; N, 4.40 %. IR νmax ($CDCl_3$) 3350, 1610 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.23 - 2.98 (13H, m, 6 x CH_2 and CH), 3.07 - 3.36 (2H, m, NCH and OCH), 3.84 (3H, s, OMe), 3.85 (3H, s, OMe), 4.73 (1H, dd, J = 5.2 and 9.2 Hz, ArCHN), 6.53 (1H, s, ArH), 6.58 (1H, s, ArH); ^{13}C NMR ($CDCl_3$) 13.4 (t), 21.1 (t), 24.9 (t), 32.8 (t), 36.2 (t), 41.8 (t), 42.2 (d), 55.4 (d), 56.0 (q), 56.1 (q), 59.0 (d), 69.4 (d), 110.0 (d), 111.2 (d), 125.3 (s), 133.1 (s), 147.2 (s), 148.3 (s); m/z 303 (*M^+*); High MS m/z 303.1826. $C_{18}H_{25}NO_3$ requires 303.1833.

Ring Closure of 8 with Phosphoric Acid A mixture of 8 (3 g) and 85 % phosphoric acid (30 ml) was heated at 100 °C for 5 h. After additon of water (50 ml), the mixture was neutralized with aqueous sodium carbonate and extracted with methylene chloride. The organic layer was washed with water, dried (Na_2SO_4) and concentrated to the residue, which was chromatographed on neutral alumina. Elution with methylene chloride afforded the cyclized product (14) (0.04 g, 1.33 %) (28.6 % based on the consumed starting material) as prisms, mp 123 - 124 °C (*n*-hexane). *Anal.* calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.52; H, 7.77; N, 4.57 %. IR νmax ($CDCl_3$) 1710, 1625 cm^{-1}; NMR δ ($CDCl_3$) 1.38 - 3.23 (15H, m, 7 x CH_2 and CH), 3.85 (6H, s, 2 x OMe), 6.52 (1H, s, ArH), 6.60 (1H, s, ArH); m/z 301 (M^+); High MS m/z 301.1669. $C_{18}H_{23}NO_3$ requires 301.1676. This compound was identical with the authentic sample derived from the known material (15) in all respects.

Ketalization of The Erythrinanone (15) A solution of 15 (3 g), ethylene glycol (0.7 g) and a catalytic amount of *p*-toluenesulfonic acid in benzene (70 ml) was refluxed with Dean-Stark equipment for 3 h. The benzene layer was washed with 10 % sodium carbonate solution and water, and dried (Na_2SO_4). Removal of the solvent afforded the amide (16) (3.4 g, 99.4 %) as a gum. IR νmax ($CHCl_3$) 1680 cm^{-1}; NMR δ ($CDCl_3$) 1.56 - 2.23 (6H, m, 3 x CH_2), 2.41 - 3.37 (7H, m, 3 x CH_2 and CH), 3.85 (3H, s, OMe), 3.89 (3H, s, OMe), 3.93 - 4.35 (4H, m, OCH_2CH_2O), 6.54 (1H, s, ArH), 7.48 (1H, s, ArH); m/z 359 (M^+); High MS m/z 359.1730. $C_{20}H_{25}NO_5$ requires 359.1731.

Reduction of The Amide (16) To a stirred suspension of $LiAlH_4$ (0.7 g) in dry tetrahydrofuran (20 ml) was added a solution of 16 (3 g) in tetrahydrofuran (50 ml) at ambient temperature over the period of 0.5 h, and the resulting mixture was refluxed for 3 h. After the usual work-up, the residue was recrystallized to give the amine (17) (2.22 g, 77 %) as needles, mp 90.5 - 91.5 °C (from *n*-hexane). *Anal.* calcd for $C_{20}H_{27}NO_4$: C, 69.54; H, 7.88; N, 4.06. Found: C, 69.33; H, 8.01; N, 4.07 %. IR νmax ($CHCl_3$) 1620 cm ; NMR δ ($CDCl_3$) 1.42 - 3.28 (15H, m, 7 x CH_2 and CH), 3.83 (3H, s, OMe), 3.86 (3H, s, OMe), 4.02 (4H, s, OCH_2CH_2O), 6.47 (1H, s, ArH), 6.97 (1H, s, ArH); m/z 345 (M^+); High MS m/z 345.1949. $C_{20}H_{27}NO_4$ requires 345.1941.

cis-Erythrinanone (14) A solution of 17 (2 g) in acetone (20 ml) and 10 % hydrochloric acid (30 ml) was stirred at ambient temperature for 4 h. After removal of the solvent, the residue was basified with saturated sodium bicarbonate solution, and extracted with methylene chloride. The methylene chloride layer was washed with water, dried (Na_2SO_4) and evaporated to give the residue, which was crystallized from n-hexane to aford 14 (1.53 g, 87.7 %) as prisms, mp 123 - 124° C, identical with the authentic specimen prepared above.

N-(6-Bromo-3,4-methylenedioxybenzyl)-2,3,4,5,6,7-hexahydroindol-4-one (19) A mixture of the bromide (18) (4.31 g), sodium iodide (10 g), dimethylformamide (20 ml) and toluene (70 ml) was refluxed for 12 h. After removal of the solvent, the residue was treated with 10 % sodium carbonate solution and extracted with benzene. The organic layer was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave the residue, which was chromatographed on neutral alumina. Elution with methylene chloride afforded the enaminone (19) (2.63 g, 75.1 %) as needles, mp 141 - 142° C (from n-hexane-acetone) (lit.,[11] mp 142 - 143 °C). IR νmax ($CHCl_3$) 1590, 1560 cm^{-1}; NMR δ ($CDCl_3$) 1.96 - 2.17 (2H, m, CH_2), 2.28 2.43 (4H, m, 2 x CH_2), 2.78 (2H, t, J = 10 Hz, $NCH_2\underline{CH_2}$), 3.49 (2H, t, J = 10 Hz, $N\underline{CH_2}CH_2$), 4.34 (2H, s, NCH_2Ar), 6.00 (2H, s, OCH_2O), 6.63 (1H, s, ArH), 7.03 (1H, s, ArH); m/z 351 ($\underline{M}^+$).

Reduction of The Enaminone (19) To a stirred suspension of $LiAlH_4$ (0.76 g) in tetrahydrofuran (20 ml) was added a solution of the enaminone (19) (3.5 g) in tetrahydrofuran (30 ml) over the period of 20 min, and the mixture was stirred for 4 h at ambient temperature. After addition of water to quench the reaction, an insoluble material was filtered off, and the filtrate was dried (Na_2SO_4) and concentrated to the residue, which was chromatographed on neutral alumina. Elution with methylene chloride gave the ketone (20) (0.59 g, 16.8 %) as needles, mp 94 - 95° C (from n-hexane). Anal. calcd for $C_{16}H_{18}BrNO_3$: C, 54.56; H, 5.15; N, 3.98. Found: C, 54.69; H, 5.15; N, 3.70 %. IR νmax ($CHCl_3$) 1700 cm^{-1}; NMR δ ($CDCl_3$) 1.58 - 2.82 (10H, m, 5 x CH_2), 2.85 - 3.11 (2H, m, 2 x CH), 3.28 (1H, d, J = 14.4 Hz, NCH_2Ar), 3.83 (1H, d, J = 14.4 Hz, NCH_2Ar), 5.94 (2H, s, OCH_2O), 6.91 (1H, s, ArH), 6.96 (1H, s, ArH); m/z 353 ($\underline{M}^+$); High MS m/z 351.0473. $C_{16}H_{18}BNO_3$ requires 351.0470. Further elution afforded the alcohol (21) (1.25 g, 35.3 %) as leaflets, mp 79.7 - 80.5 (from n-hexane). Anal. calcd for $C_{16}H_{20}BrNO_3$: C, 54.25; H, 5.69; N, 3.95. Found: C, 54.29; H, 5.72; N, 3.67 %. IR νmax ($CHCl_3$) 3350 cm^{-1}; NMR δ ($CDCl_3$) 1.17 - 2.25 (10H, m, 5 x CH_2), 2.53 (1H, m, CH), 2.85 - 2.98 (1H, m, NCH), 2.99 (1H, d J = 12.6 Hz, NCH_2Ar), 3.68 (1H, m, $\underline{CH}OH$), 4.00 (1H, d, J = 12.6 Hz, NCH_2Ar), 4.67 (1H, br s, OH), 5.96 (2H, s,

OCH_2O), 6.78 (1H, s, ArH), 6.99 (1H, s, ArH); m/z 353 (M+); High MS m/z 353.0615. $C_{16}H_{20}BrNO_3$ requires 353.0616.

Alternative Synthesis of 20 A solution of 3-aziridinocyclohexan-1-one (23) (4.17 g) and 6-bromo-3,4-methylenedioxybenzyl bromide (8.46 g) in dry benzene (100 ml) was heated under reflux for 12 h. After cooling to room temperature, potassium *tert*-butoxide (3.37 g) was added and the resulting mixture was again refluxed for 2 h. The organic layer was washed with water and dried (Na_2SO_4). Evaporation of the solvent afforded the residue, which was crystallized to give 20 (7.69 g, 72.8 %) as needles, mp 94 - 95 °C (from *n*-hexane). This compound was identical with the authentic sample obtained above.

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