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A Convenient Synthesis of 1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-*a*]quinolizine Derivatives[1)]

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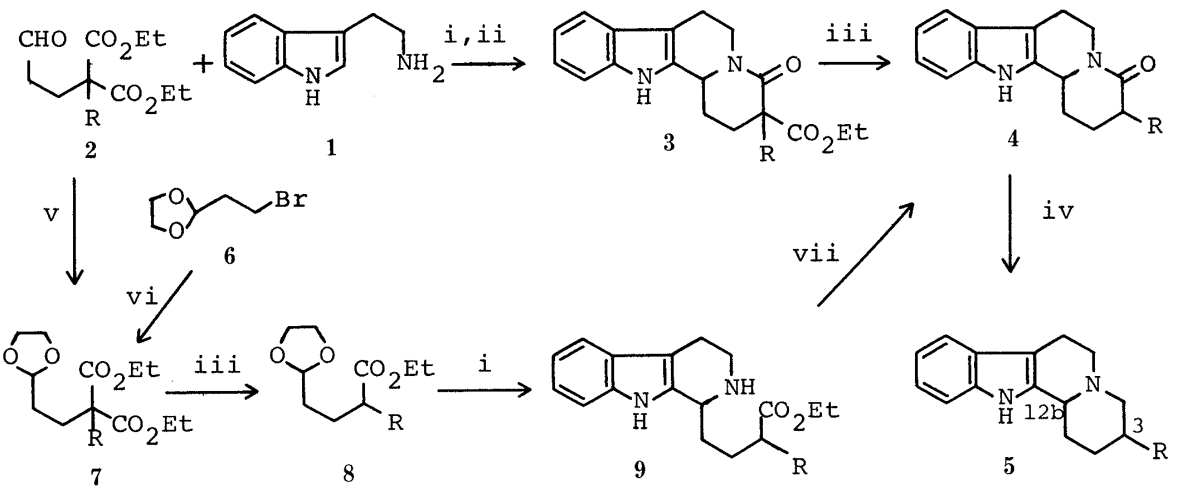
Convenient syntheses of 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine derivatives (**4a**, **b**) and a related unsaturated lactam (**14**) are described. The condensation of tryptamine (**1**) with **8a**, **b** (prepared from **7a**, **b** by decarboethoxylation), followed by treatment with alkali gave the lactams (**4a**, **b**), respectively. The stereochemistry of **4b** was determined by conversion to the known *cis*- and *trans*-compounds (**5b**). The condensation of **1** with the sulfenylated ester (**10**), which was prepared in two ways, followed by treatment with alkali gave the lactams (**12a**, **b**). Oxidation of **12a**, **b** with *m*-chloroperbenzoic acid gave the sulfoxides (**13**) which were heated at 50 °C to give the lactams (**14**, **15**) and the pyridone (**16**).

Keywords——indole; synthesis; indolo[2,3-*a*]quinolizine; Pictet–Spengler reaction; dehydrosulfenylation

Previously we reported[1)] a synthesis of the indoloquinolizidine (**5a**) from tryptamine (**1**) and the aldehyde (**2a**) through the intermediates **3a** and **4a**. The method involved decarboethoxylation after Pictet–Spengler condensation of **1** with **2a** (Chart 1). If the decarboethoxylation could be done before the condensation, the synthetic procedure would be easier and simpler. In the present paper, we describe a modification of our synthetic route to **5a**, **b** and the preparation of the unsaturated lactam (**14**). Since our previous paper, other synthetic methods for **5a** have been reported.[2)]

The monoester (**8a**) was considered to be the aldehyde equivalent of **2a**. The acetal (**7a**), which had been prepared[3)] by acetalization of **2a**, was prepared by condensation of diethyl malonate with the bromide (**6**) in the presence of NaOEt. The acetal (**7a**) was then treated with lithium chloride (LiCl)–dimethyl sulfoxide (Me_2SO)–water[4)] to give the monoester (**8a**, 70%). Pictet–Spengler reaction of tryptamine (**1**) with **8a** was carried out in 80% aq. acetic acid (AcOH) at 60—70 °C followed by treatment with ethanolic potassium hydroxide (KOH) to give the lactam (**4a**, 78%). The intermediate (**9a**) could be isolated by working up the reaction mixture before treatment with alkali. The structure of **9a** was supported by the following data [proton nuclear magnetic resonance (^{1}H-NMR) spectrum (100 MHz, Me_2SO-d_6) δ: 1.18 (3H, t, $J=7$ Hz), 4.04 (2H, q-like). Infrared (IR) spectrum (KBr): 1730 cm^{-1}. Mass spectrum (MS) *m/z* (%): 286 (M^+, 18), 171 (100)] and the observation that this compound was easily converted to the lactam (**4a**) on heating. The lactam (**4a**) had previously been reduced to **5a**.[1)]

The above synthetic route was applied to the preparation of 3-ethylindoloquinolizidine (**5b**). The preparation of the monoester (**8b**) has been reported[5)] from **7b**, which was prepared by condensation of diethyl ethylmalonate with the bromide (**6**) in the presence of sodium ethoxide (NaOEt)[5)] or by acetalization of **2b**. The condensation of tryptamine (**1**) with the monoester (**8b**) was carried out in the same manner as in the case of **8a** to give the less polar lactam (*trans*-**4b**, 35%) and the more polar lactam (*cis*-**4b**, 30%). The stereochemistry of the lactams (**4b**), which remained undetermined in the earlier work,[1)] was now determined by



a series: R = H **b** series: R = Et

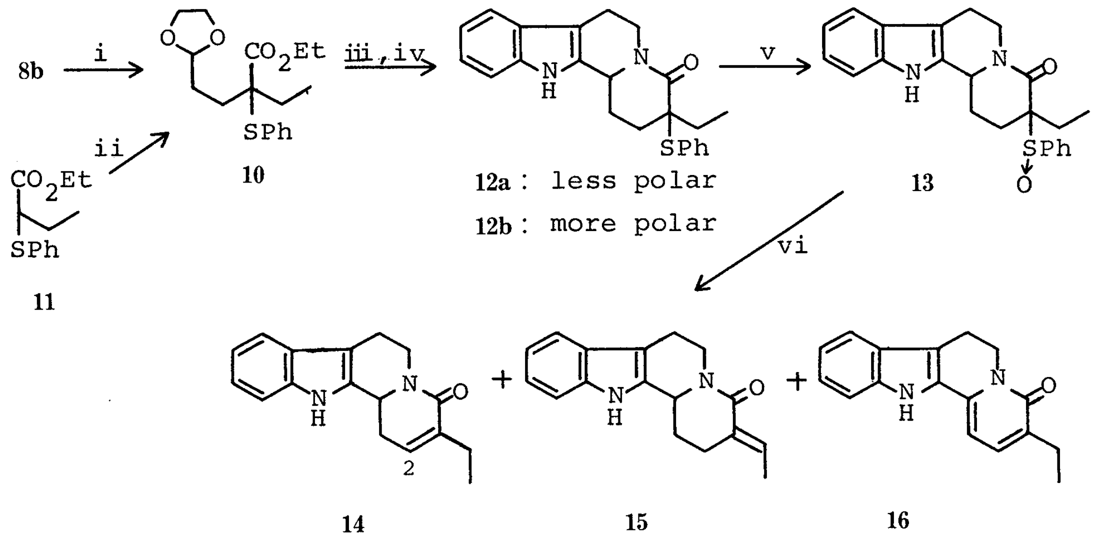
i) **1**, 80% aq. AcOH ii) 20% aq. K_2CO_3–EtOH iii) LiCl/Me_2SO/H_2O

iv) $LiAlH_4$/THF v) $HOCH_2CH_2OH$/TsOH vi) $RCH(CO_2Et)_2$/NaOEt

vii) KOH–EtOH

Chart 1

conversion to the known *cis*- and *trans*-compounds (**5b**). The *trans*- and *cis*-lactams (**4b**) were reduced with lithium aluminium hydride ($LiAlH_4$) in refluxing tetrahydrofuran (THF) to give *trans*-**5b** (90%, mp 160—161 °C, lit.[6] mp 163—165 °C) and *cis*-**5b** (80%, picrate: mp 214—217 °C, lit.[6] mp 220—224 °C), respectively. The ^{1}H-NMR spectrum of *cis*-**5b** showed the signal due to H-12b at δ 3.72 at a characteristically deshielded position, as reported in the literature.[6] The *trans* configuration of the other compound (**5b**) obtained from the less polar lactam (**4b**) was further confirmed by its carbon-13 nuclear magnetic resonance (^{13}C-NMR) data, which were identical with the reported data[7] within ± 0.2 ppm.



i) PhSSPh–LDA/HMPA–THF ii) **6**, LDA/HMPA–THF iii) **1**, 80% aq. AcOH

iv) KOH–EtOH v) MCPBA vi) 50 °C/CCl_4

Chart 2

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The above route was further applied to a preparation of the unsaturated lactam (**14**), which may be a useful intermediate[1] for the synthesis of *Corynanthé* alkaloids. The sulfenylated ester (**10**) was prepared in two ways: a) treatment of the monoester (**8b**) with PhSSPh in the presence of lithium diisopropylamide (LDA) in THF–hexamethylphosphoramide (HMPA)[8] to give **10** (75%); b) condensation of **11** with the bromide (**6**) in the presence of LDA in THF–HMPA to give **10** (70%). Pictet–Spengler reaction of tryptamine (**1**) with the sulfide (**10**) in refluxing 80% aq. AcOH followed by treatment with ethanolic KOH gave the less polar lactam (**12a**, 18%) and the more polar lactam (**12b**, 50%). No attempt was made to determine the configuration of the two lactams (**12**).

Oxidation of the less polar lactam (**12a**) with *m*-chloroperbenzoic acid (MCPBA) gave the corresponding sulfoxide (**13**) in good yield. Without further purification, the sulfoxide (**13**) was heated in CCl_4 at 50 °C to give the desired compound (**14**, 78%) together with the lactam (**15**, 3%) and the pyridone (**16**, 3%). Dehydrosulfenylation of the more polar lactam (**12b**) was performed in the same manner to give **14** (58%), **15** (21%) and **16** (2%). The structures of the products (**14**, **15**, **16**) were confirmed by their spectral data, and the *E* configuration of double bond in the lactam (**15**) was deduced from the ^{1}H-NMR data as follows. The chemical shift values due to the ethylidene group at δ 1.73 ($C=CH-C\underline{H}_3$) and δ 6.76 ($C=C\underline{H}-CH_3$) were identical with those (δ 1.71 and 6.79) reported.[9] The ultraviolet (UV) spectrum of **16** was similar to that of the skeletal compound (deethyl derivative),[10] confirming the structure.

Michael addition of dimethyl malonate, methyl (phenylthio)acetate, or 2-methoxycarbonyl-1,3-dithiolane to the C-2 position of the lactam (**14**) was attempted in the hope of synthesizing *Corynanthé* alkaloids, but all attempts were unsuccessful.

Experimental

All melting points were measured on a Yamato MP-21 apparatus and are uncorrected. Boiling points are also uncorrected. IR spectra were measured with a Hitachi 260 spectrometer, and UV spectra were measured in MeOH with a Hitachi 340 spectrometer. ^{1}H-NMR spectra were recorded on Hitachi R-24B (60 MHz), JEOL JNM4H-100 (100 MHz), and FX-270 (270 MHz) spectrometers with tetramethylsilane (TMS) as an internal standard in $CDCl_3$ unless otherwise stated. ^{13}C-NMR spectra were measured with a JEOL FX-270 (67.8 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard. MS were taken with Hitachi RMU 7M and 60 spectrometers. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60F-254 plates. Column chromatography utilized Merck silica gel (70—230 and 230—400 mesh). Organic solutions were dried with anhydrous Na_2SO_4. Abbreviations used are: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), shoulder (sh).

Diethyl (2-Formylethyl)malonate Ethylene Acetal (7a)——Diethyl malonate (7.70 g) was added dropwise over 5 min to a NaOEt solution [prepared from Na (1.07 g) and dry EtOH (30 ml)] at 50 °C, and then 2-(2-bromoethyl)-1,3-dioxolane (**6**) (8.46 g) was added over 5 min at 50 °C. The mixture was refluxed for 4 h, and then concentrated, diluted with water and extracted with ether. The organic layer was washed with water, dried and concentrated. The residue was distilled to give **7a** (8.30 g, 68%), bp 130—136 °C (2 mmHg) [lit.[3] bp 150 °C (5 mmHg)]. ^{1}H-NMR (60 MHz, CCl_4) δ: 1.27 (6H, t, $J=7$ Hz), 1.77 (4H, m), 3.26 (1H, t, $J=7$ Hz), 3.82 (4H, m), 4.14 (4H, q, $J=7$ Hz), 4.77 (1H, t, $J=4$ Hz). The ^{1}H-NMR spectrum of **7a** was identical with that of an authentic sample prepared by the reported procedure.[3]

Ethyl 4-Formylbutyrate Ethylene Acetal (8a)——LiCl (3.34 g) and H_2O (0.66 ml) were added to a solution of **7a** (10.0 g) in Me_2SO (66 ml) and the mixture was refluxed for 3 h under argon, then poured into brine and extracted with hexane. The extract was washed with brine, dried, and concentrated. The residue was distilled to give the monoester (**8a**) (5.07 g, 70%), bp 96—99 °C (4 mmHg). An analytical sample was redistilled: bp 103 °C (5 mmHg). MS *m/z* (%): 188 (M^+, 0.3), 73 (100). ^{1}H-NMR (60 MHz, CCl_4) δ: 1.24 (3H, t, $J=7$ Hz), 1.5—1.8 (4H, m), 2.26 (2H, m), 3.80 (4H, m), 4.05 (2H, q, $J=7$ Hz), 4.75 (1H, t, $J=4$ Hz). *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 56.91; H, 8.69.

1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-*a*]quinolizin-4-one (4a)——A solution of tryptamine (**1**) (1.61 g) and the monoester (**8a**) (2.27 g) in AcOH (62 ml) and H_2O (15 ml) was heated at 60—70 °C for 4 h with stirring under argon. The mixture was concentrated under reduced pressure. A solution of KOH (3.30 g) in EtOH (120 ml) was added to the residue and the mixture was stirred overnight at room temperature (RT) under argon. The resultant crystalline precipitate was collected by filtration and washed with EtOH to give the lactam (**4a**) (1.39 g, mp 235—243 °C). The filtrate was concentrated, diluted with water and extracted wih $CHCl_3$. The organic layer was washed with brine and

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dried. Removal of the solvent followed by crystallization from EtOH gave **4a** (0.49 g, mp 238—242 °C); total yield: 1.88 g (78%). The IR spectrum and TLC behavior of **4a** were identical with those of an authentic sample.[1)]

Diethyl Ethyl(2-formylethyl)malonate Ethylene Acetal (7b)——A solution of the aldehyde (**2b**) (14.1 g) and ethylene glycol (4.32 g) in dry benzene (70 ml) was refluxed for 5 h in the presence of *p*-TsOH (10 mg) with a Dean–Stark trap. The mixture was washed with 5% aq. $NaHCO_3$, dried and concentrated. The residue was purified by distillation to give the acetal (**7b**) (11.35 g, 68%), bp 146—150 °C (4 mmHg). An analytical sample was redistilled: bp 142 °C (3 mmHg). MS *m/z* (%): 288 (M^+, 1), 99 (100). ^1H-NMR (60 MHz, CCl_4) δ: 0.79 (3H, t, $J=7$ Hz), 1.22 (6H, t, $J=7$ Hz), 1.4—2.1 (6H, m), 3.80 (4H, m), 4.11 (4H, q, $J=7$ Hz), 4.72 (1H, t, $J=4$ Hz). *Anal.* Calcd for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 58.18; H, 8.34.

Ethyl 2-Ethyl-4-formylbutyrate Ethylene Acetal (8b)——Decarboethoxylation of **7b** (9.23 g) was carried out by the procedure used in the conversion of **7a** to **8a** with LiCl (2.71 g), H_2O (0.58 ml) and Me_2SO (50 ml). The crude product was distilled to give the monoester (**8b**) (5.78 g, 83%), bp 112—121 °C (5 mmHg). An analytical sample was redistilled: bp 115 °C (5 mmHg). MS *m/z* (%): 216 (M^+, 1), 73 (100). ^1H-NMR (60 MHz, CCl_4) δ: 0.87 (3H, t, $J=7$ Hz), 1.22 (3H, t, $J=7$ Hz), 1.4—1.8 (6H, m), 2.15 (1H, m), 3.78 (4H, m), 4.05 (2H, q, $J=7$ Hz), 4.70 (1H, m). *Anal.* Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.94; H, 9.40.

3-Ethyl-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-4-one (4b)——A solution of **1** (320 mg) and **8b** (520 mg) in AcOH (10 ml) and H_2O (2.5 ml) was heated at 60—70 °C for 4 h. The mixture was concentrated and a solution of KOH (0.66 g) in EtOH (25 ml) was added to the residue. The mixture was stirred overnight at RT, and then concentrated, diluted with water, and extracted with $CHCl_3$. The extract was washed with brine, dried and concentrated. The residue was chromatographed on SiO_2 (20 g). Eluates with benzene–EtOAc (8 : 2) gave the less polar lactam (*trans*-**4b**) (190 mg, 35%, mp 201—203 °C). ^{13}C-NMR δ: 11.3 (q), 21.1 (t), 24.5 (t), 24.9 (t), 28.7 (t), 40.4 (t), 43.3 (d), 54.7 (d), 109.1 (s), 111.0 (d), 118.3 (d), 119.6 (d), 121.9 (d), 126.8 (s), 133.8 (s), 136.4 (s), 172.0 (s).

Eluates with benzene–EtOAc (1 : 1)—EtOAc gave the more polar lactam (*cis*-**4b**) (160 mg, 30%, mp 203—205 °C). ^{13}C-NMR δ: 12.1 (q), 21.1 (t), 22.5 (t), 25.0 (t), 25.3 (t), 40.7 (t), 42.7 (d), 54.5 (d), 109.4 (s), 111.0 (d), 118.3 (d), 119.7 (d), 122.0 (d), 126.9 (s), 133.6 (s), 136.3 (s), 172.8 (s).

The IR spectra and TLC behavior of the lactams (**4b**) were identical with those of corresponding authentic samples.[1)]

***trans*-3-Ethyl-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine (5b)**——A solution of *trans*-**4b** (134 mg) in dry THF (7 ml) was added dropwise to a suspension of $LiAlH_4$ (76 mg) in dry THF (3 ml) in an ice bath and the mixture was refluxed for 2 h. After cooling, anhydrous Na_2SO_4 (0.1 g) was added and aq. THF was added to the mixture to decompose the excess $LiAlH_4$. The mixture was filtered and the filtrate was concentrated to give the residue which was chromatographed on Al_2O_3 (1 g). Eluates with $CHCl_3$ gave *trans*-**5b** (114 mg, 90%). mp 158—160 °C (MeOH–H_2O). An analytical sample was recrystallized from MeOH–H_2O. mp 160—161 °C (lit.[6)] mp 163—165 °C). *Anal.* Calcd for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.23; H, 8.62; N, 10.96.

***cis*-3-Ethyl-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine (5b)**——Reduction of *cis*-**4b** (134 mg) with $LiAlH_4$ (76 mg) was carried out in the same way as for *trans*-**4b**. The crude product was purified by short-column Al_2O_3 chromatography (1 g) with $CHCl_3$ to give *cis*-**5b**, which was characterized as the picrate (180 mg, 80%). mp 214—217 °C (MeOH). (lit.[6)] mp 220—224 °C). *Anal.* Calcd for $C_{23}H_{25}N_5O_7$: C, 57.13; H, 5.21; N, 14.49. Found: C, 56.88; H, 5.23; N, 14.46. Free base: ^{13}C-NMR δ: 11.9 (q), 19.5 (t), 25.6 (t), 26.5 (t), 27.2 (t), 36.9 (d), 52.7 (t), 55.7 (t), 57.4 (d), 108.0 (s), 110.8 (d), 118.0 (d), 119.3 (d), 121.2 (d), 127.6 (s), 134.4 (s), 135.8 (s).

Ethyl 2-Ethyl-4-formyl-2-(phenylthio)butyrate Ethylene Acetal (10)——a) The monoester (**8b**) (3.07 g) was added dropwise over 10 min to a solution of LDA prepared from diisopropylamine (2.00 ml) and *n*-BuLi (1.6 M in hexane, 8.87 ml) in dry THF (12 ml) at −70 °C, and the mixture was stirred for 1 h. After removal of the cooling bath, a solution of PhSSPh (3.71 g) in a mixture of HMPA (2.95 ml) and dry THF (6 ml) was added and the whole was stirred for 1 h at RT. The mixture was poured into EtOAc (60 ml) and the organic layer was washed successively with 2 N HCl and saturated aq. $NaHCO_3$. The organic layer was dried and concentrated to give the residue, which was subjected to SiO_2 (100 g) chromatography. Eluates with benzene–EtOAc (9 : 1) gave the sulfide (**10**) (3.44 g, 75%). An analytical sample was distilled. bp 158—160 °C (0.4 mmHg). MS *m/z* (%): 324 (M^+, 40), 251 (58), 169 (100). ^1H-NMR (60 MHz, CCl_4) δ: 0.91 (3H, t, $J=7$ Hz), 1.16 (3H, t, $J=7$ Hz), 1.45—2.0 (6H, m), 3.75 (4H, m), 4.01 (2H, q, $J=7$ Hz), 4.70 (1H, m), 7.05—7.50 (5H, m). *Anal.* Calcd for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46. Found: C, 63.13; H, 7.33.

b) A solution of ethyl 2-(phenylthio)butyrate (**11**) (600 mg) in a mixture of HMPA (0.67 ml) and dry THF (0.5 ml) was added dropwise to a solution of LDA [prepared from diisopropylamine (0.49 ml) and *n*-BuLi (1.6 M in hexane, 2.18 ml)] in dry THF (3 ml) at −70 °C, and the mixture was stirred for 5 min, then for further 20 min in an ice bath. The mixture was recooled to −70 °C, and a solution of the bromide (**6**) (630 mg) in dry THF (0.5 ml) was added dropwise over 10 min. The cooling bath was removed and the mixture was stirred for 4 h. The mixture was poured into saturated NH_4Cl (20 ml) and extracted with EtOAc. The organic layer was washed with brine, dried, and concentrated. The residue was chromatographed on SiO_2 (30 g). Eluates with benzene–EtOAc (1 : 1) gave the sulfide (**10**, 608 mg, 70%).

3-Ethyl-3-phenylthio-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-4-one (12)——A solution of tryptamine (**1**) (1.21 g) and the sulfide (**10**) (2.93 g) in AcOH (30 ml) and H_2O (7.5 ml) was refluxed for 2 h under argon. The

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solvent was evaporated off, and a solution of KOH (2.53 g) in EtOH (40 ml) was added to the residue. The mixture was stirred for 2 h at RT. The resultant precipitate was collected by filtration and washed with EtOH to give an epimeric mixture of lactams (**12a, b**) (1.69 g), which was chromatographed on SiO_2 (50 g). Eluates with 2% EtOAc–benzene gave the less polar lactam (**12a**) (41 mg). Eluates with 3—5% EtOAc–benzene gave the more polar lactam (**12b**) (1.31 g). The filtrate was concentrated, diluted with water, and extracted with $CHCl_3$. The organic layer was washed with water, dried, and concentrated. The residue was chromatographed on SiO_2 (50 g) to give **12a** [0.46 g, 191—194 °C (ether)] and **12b** [87 mg, mp 217—223 °C (ether)]. The less polar lactam (**12b**): total yield 0.50 g (18%). mp 197—199 °C (acetone). MS *m/z* (%): 376 (M^+, 4), 267 (48), 266 (100), 251 (86). UV $\lambda_{\max}$ nm (log ε): 225 (4.71), 274 (3.98), 280 (sh, 3.97), 290 (3.85). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300, 1620. ^{1}H-NMR (100 MHz) δ: 0.90 (3H, t, $J=7$ Hz), 4.52 (1H, m), 5.05 (1H, m), 7.0—7.7 (9H, m), 8.18 (1H, br s, NH). *Anal.* Calcd for $C_{23}H_{24}N_2OS$: C, 73.37; H, 6.42; N, 7.44. Found: C, 73.34; H, 6.38; N, 7.21. The more polar lactam (**12b**): total yield 1.40 g (50%). mp 221—224 °C (MeOH). MS *m/z* (%): 376 (M^+, 100), 267 (100), 266 (59). UV $\lambda_{\max}$ nm (log ε): 224 (4.71), 274 (3.97), 281 (sh, 3.96), 290 (3.83). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3360, 1620. ^{1}H-NMR (100 MHz, Me_2SO-d_6) δ: 0.87 (3H, t, $J=7$ Hz), 4.80 (2H, m), 6.8—7.5 (9H, m), 10.84 (1H, br s, NH). *Anal.* Calcd for $C_{23}H_{24}N_2OS$: C, 73.37; H, 6.42; N, 7.44. Found: C, 73.13; H, 6.43; N, 7.21.

Dehydrosulfenylation of the Less Polar Lactam (12a)——A solution of MCPBA (290 mg, 80% purity) in dry $CHCl_3$ (5 ml) was added dropwise to a solution of **12a** (460 mg) in dry $CHCl_3$ (17 ml) in an ice bath. The mixture was stirred for 30 min at RT and then poured into a mixture of $CHCl_3$ (80 ml) and 10% aq. Na_2SO_3 (80 ml). The whole was shaken well, then the organic layer was washed with 5% aq. $NaHCO_3$, dried and concentrated to give the sulfoxide (**13**) (475 mg).

A solution of the sulfoxide (**13**) in CCl_4 (5 ml) was heated for 3 h at 50 °C. The mixture was diluted with $CHCl_3$, washed with brine, dried and concentrated. The residue was chromatographed on SiO_2 (10 g). Eluates with 6% EtOAc–benzene gave 3-ethyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizin-4-one (**14**) (252 mg, 78%). mp 219—223 °C (ether). An analytical sample was recrystallized from acetone. mp 226—227 °C. MS *m/z* (%): 266 (M^+, 100), 265 (37). UV $\lambda_{\max}$ nm (log ε): 223 (4.63), 273 (3.96), 282 (sh, 3.93), 290 (3.81). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1660, 1600. ^{1}H-NMR (270 MHz) δ: 1.10 (3H, t, $J=7.5$ Hz), 2.3—2.5 (3H, m), 2.6—3.0 (4H, m), 4.81 (1H, dd, $J=13.5$, 4.5 Hz), 5.07 (1H, m), 6.37 (1H, d, like $J=5$ Hz), 7.1—7.6 (4H, m), 7.90 (1H, br s, NH). *Anal.* Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.57; H, 6.72; N, 10.46.

Eluates with 20% EtOAc–benzene gave 3-ethyl-4,6,7,12-tetrahydroindolo[2,3-*a*]quinolizin-4-one (**16**) (11 mg, 3%). mp 247—250 °C (ether). UV $\lambda_{\max}$ nm: 252, 261, 278, 291, 352 (sh), 367, 386. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1640, 1560, 1540. ^{1}H-NMR (270 MHz) δ: 1.22 (3H, t, $J=7.5$ Hz), 2.63 (2H, q, $J=7.5$ Hz), 3.10 (2H, t, $J=7$ Hz), 4.49 (2H, t, $J=7$ Hz), 6.35 (1H, d, $J=7.3$ Hz), 7.1—7.7 (5H, m), 8.51 (1H, br s, NH). High resolution MS Calcd for $C_{17}H_{16}N_2O$: 264.1262. Found: 264.1234.

Elution with 20—30% EtOAc–benzene followed by crystallization of the product from ether gave 3-(*E*)-ethylidene-1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizin-4-one (**15**) (9 mg, 3%). mp 232—235 °C. An analytical sample was recrystallized from acetone. mp 235—237 °C (lit.[9] mp 245 °C). ^{1}H-NMR (270 MHz, Me_2SO-d_6) δ: 1.73 (3H, dd, $J=7.3$, 1.7 Hz), 6.76 (1H, qd, $J=7.3$, 1.7 Hz). *Anal.* Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.48; H, 6.75; N, 10.51.

Dehydrosulfenylation of the More Polar Lactam (12b)——A solution of MCPBA (396 mg, 80% purity) in dry $CHCl_3$ (5 ml) was added to a solution of **12b** (564 mg) in dry $CHCl_3$ (25 ml) in an ice bath, and the mixture was stirred overnight at RT. Work-up was carried out in the same way as described above for the less polar lactam. The residue was dissolved in CCl_4 (4 ml) and the mixture was heated for 3 h at 50 °C. Work-up was carried out as before, and the crude product was chromatographed on SiO_2 (15 g) to give the lactam (**14**) (230 mg, 58%), the pyridone (**16**) (9 mg, 2%), and the lactam (**15**) (83 mg, 21%).

References and Notes

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