Synthesis of a Pentacyclic Precursor to the Strychnos Alkaloids

George A. Kraus,* P. J. Thomas, Dan Bougie, and Li Chen

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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An advanced intermediate for the synthesis of the Strychnos alkaloids was constructed by a sequence involving an intramolecular Diels-Alder reaction, alkylation of an enol silyl ether, and conversion of the alkylation product into a pentacyclic lactam.

The indole alkaloids comprise a diverse group of medicinally significant and structurally complex natural products.[1] Compounds such as vinblastine, a dimeric indole alkaloid with useful anticancer activity, and eburnamine have encouraged continued synthetic interest in indole alkaloids. From the pioneering efforts of Woodward,[2] Stork,[3] and Büchi[4] to the recent elegant studies of Magnus,[5] Kuehne,[6] and Martin,[7] many creative and useful strategies have been developed. Nevertheless, the interest in direct pathways to these complex alkaloids remains intense.[8] We recently reported a route to indole alkaloids based on an intramolecular Diels-Alder reaction using the indole C2-C3 bond as a dienophile.[9] We now report a related tack which involves the indole C2-C3 bond as part of the diene subunit. This tack should permit a facile entry to the Strychnos alkaloids. In the last few years several researchers have communicated syntheses of tetracyclic intermediates for the synthesis of the Strychnos alkaloids.[10]

The retrosynthetic analysis, depicted in Scheme I, features three key carbon-carbon bond forming reactions: the intramolecular Diels-Alder reaction, the alkylation of the enol silyl ether, and the conjugate addition. This latter reaction poses the most challenging stereochemical problems.

Intramolecular Diels-Alder reactions on alkenyl indoles have good precedent. Many examples using 2-alkenylindoles have been recorded, the most notable being the reactions developed by the Kuehne group in the context of their clever syntheses of the Aspidosperma alkaloids. Surprisingly, only a few reactions using 3-alkenylindoles have been reported.[11]

Our synthesis of enol silyl ether **2** is shown in Scheme II. The N-acylation of 3-acetylindole afforded the amide ester in 79% yield. Interestingly, a slight excess of indole had to be used, since O-acylation of the resulting amide was a competing reaction with excess acid chloride. This unexpected reactivity of the amide moiety will also limit our choice of reagents in subsequent steps.

Although attempted formation of the enol silyl ether with LDA/TMSCl at -78 °C led to a mixture of products, the enol silyl ether could be generated with TMSOTf and diisopropylethylamine. The unpurified material was sufficiently pure to be taken on to the thermolysis step. After several experiments, the optimal conditions for the Diels-Alder reaction were determined to be 270 °C for 48 h. The resulting tetracyclic enol silyl ether **2** was stable to flash chromatography. The methine protons in **2** are trans, as evidenced by a coupling constant of 10 Hz. Compound **2** could be readily hydrolyzed to ketone **5**, which was always accompanied by small amounts of indole-containing impurities.

With **2** in hand, alkylation became the next key bond-forming step. The alkylation of enol silyl ethers is a well-documented reaction, affording products under either Lewis acid mediated or fluoride-mediated conditions.[12] The reaction of **2** with allyl bromide and dry tetrabutylammonium fluoride afforded only O-alkylated product. This product could not be isomerized via a Claisen rearrangement to **6** (R, R′ = H). Recently, Gramain and Husson achieved the successful C-alkylation of a related enolate generated by KH.[13] The reaction of **2** with titanium tetrachloride and 1-chloro-3-methyl-2-butene (**7**) at temperatures ranging from -78 °C to 0 °C generated ketone **5** with only traces of **6** (R, R′ = Me) (Scheme III). The same result was true of the alkylation reaction with 1-chloro-3-phenyl-2-butene (**8**). Ether **9** could be generated in 88% yield by the reaction of **2** with titanium tetrachloride and chloromethyl methyl ether. Unfortunately, efforts to extend this reaction to more useful halides such as **10** failed.

With this avenue closed, we reconsidered the reaction of **2** with allylic chlorides. Inspection of molecular models indicated that steric hindrance was not responsible for the failure of this reaction. However, the combined inductive effects of the aryl and lactam moieties may be attenuating the reactivity of the enol silyl ether, permitting loss of a proton from the cation derived from **7** or **8** to effectively compete with alkylation. If this consideration was true, then 1-chloro-3,3-diphenyl-2-propene (**11**)[14] might afford a good yield of alkylation product. In the event, reaction of **2** with **11** and stannic chloride provided a 93% isolated yield of product **6** (R, R′ = Ph). Alcohol **12**, the precursor to **11**, afforded a 80% yield of **6** (R, R′ = Ph).

We briefly examined the reaction of **11** with representative enol silyl ethers using exactly the same reaction

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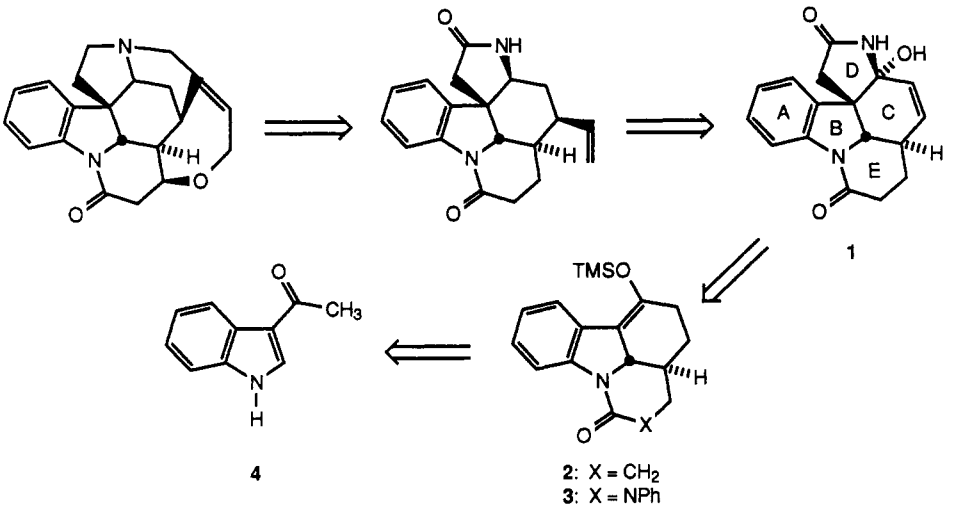
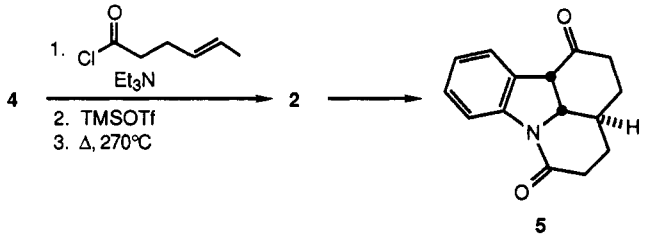
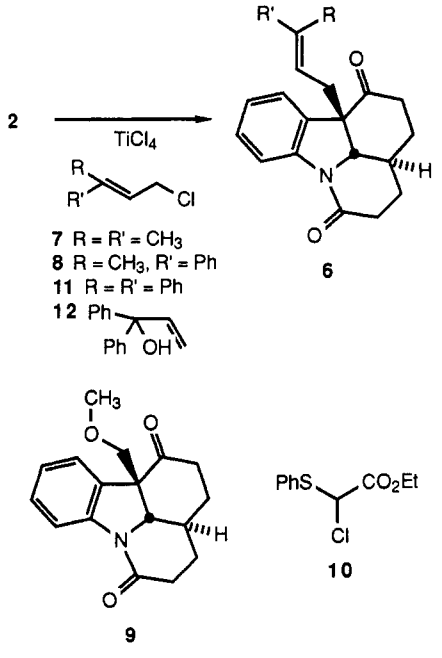
Scheme I



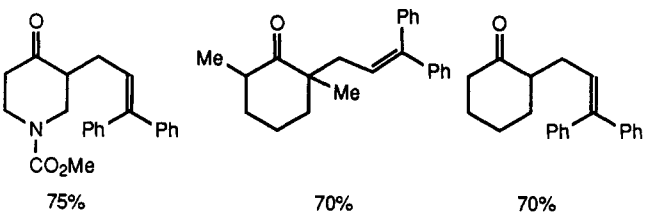
Scheme II



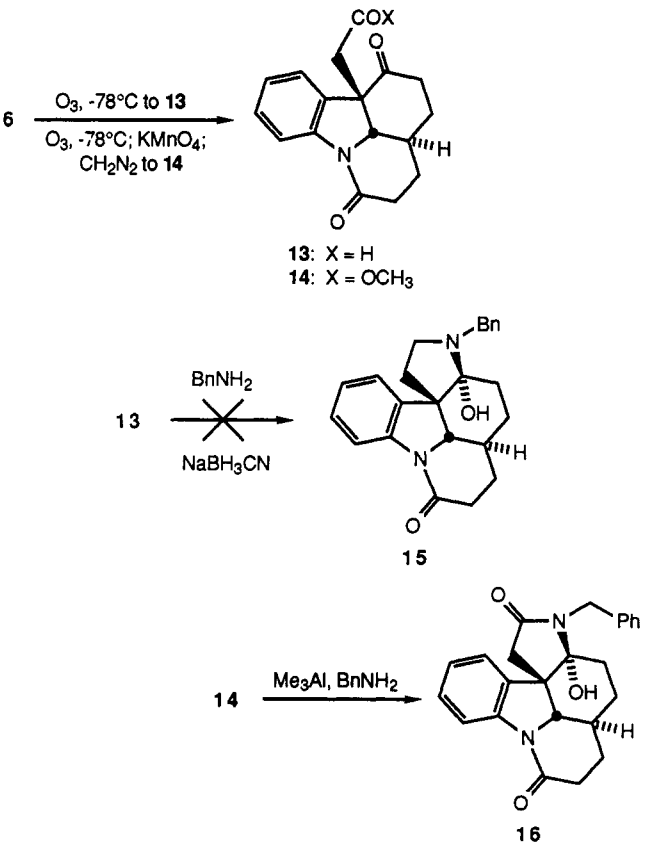
Scheme III



Scheme IV



Scheme V



conditions. The results are depicted in Scheme IV. One limitation is competing alkylation of the aromatic rings of the diphenylpropenyl unit. This is not a severe limitation, because the alkene is usually cleaved in a subsequent step to generate an aldehyde or acid. Chloride **11** may become the reagent of choice with relatively unreactive enol silyl ethers.

The appendage of the D ring might be accomplished through the intermediacy of either aldehyde **13** or ester **14**. Keto aldehyde **13** was prepared by the low-temperature ozonolysis of **6** (R, R′ = Ph) (Scheme V). Reductive amination of **13** with benzylamine and sodium cyanoborohydride was examined with the intent of obtaining amine **15**. While selective reductive amination reactions with dicarbonyl compounds are rare,[15] we anticipated that amino alcohol **15** might be stable to further reduction since the immonium salt generated by loss of water was a

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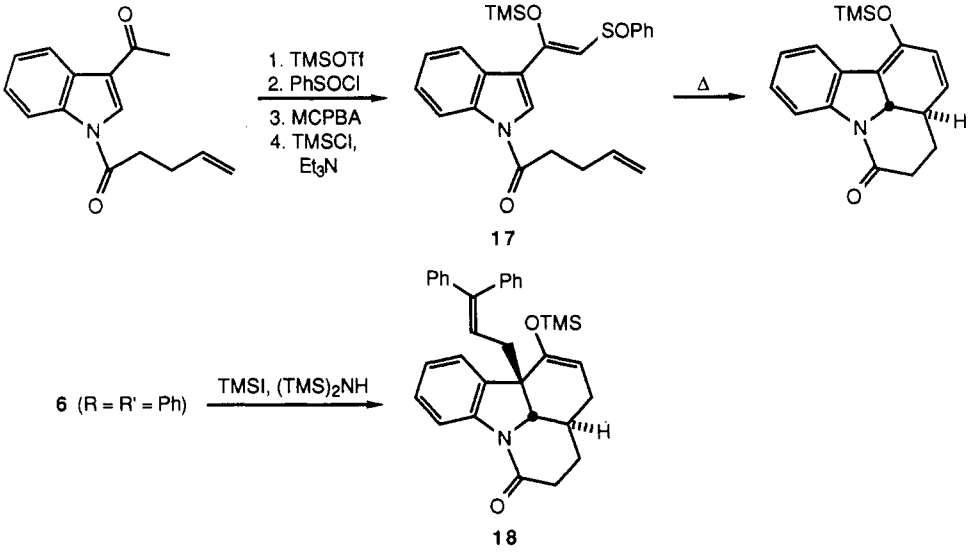
Scheme VI



strained bridgehead intermediate. Unfortunately, this reaction produced several products and was not reproducible. Ester **14** could be prepared from aldehyde **13** in 85% yield by permanganate oxidation[16] to the acid followed by esterification with diazomethane. Reaction of ester **14** with the reagent formed from trimethylaluminum and benzylamine afforded the crystalline hydroxy lactam **16** in 42% yield.

Support for the presence of the hydroxylactam subunit came from infrared absorptions at 3360 and 1700 cm^{-1}, the presence of a carbon resonance at 93 ppm (N–C–O) and the absence of a resonance in the ketone region of the ^{13}C NMR. Support for the cis-BC ring juncture came from NOE difference spectroscopy, wherein irradiation of the endo methylene proton adjacent to the carbonyl of five-membered ring lactam produced a 12.9% enhancement of the methine proton at the BC ring juncture. The 10.3-Hz coupling constant for the methine proton at 3.40 strongly supports a trans-CE ring juncture.

The introduction of the alkene in ring C was examined at several stages. We initially sought to generate the alkene during the Diels–Alder reaction, as shown in Scheme VI. While initially promising, problems associated with the preparation of sulfoxide **17** of sufficient purity for the Diels–Alder reaction caused us to delay introduction of the alkene until a later stage. Ketone **6** was also a logical point for enone formation. Reaction of **6** with LDA/TMSCl produced a mixture of enol silyl ethers from both the ketone and the amide. This was also true with TMSOTf and diisopropylamine. Fortunately, the reaction of **6** with TMSI and hexamethyldisilazane produced the desired enol silyl ether **18**.[17]

At this point **18** was treated with several electrophilic reagents (PhSeCl, PhSeBr, Br_2, NBS and PhSCl). The enol silyl ether was consumed, but the recovery of purified products after chromatography was poor. A likely explanation is that the 1,1-diphenylpropenyl moiety is also reacting, either directly with the electrophile or with the byproducts of the electroplilic attack on the enol silyl ether (e.g. TMSCl or TMSBr). Unexpectedly, the use of palladium reagents such as $Pd(OAc)_2$[18] or Pd(0)/diallyl-carbonate[19] gave recovered starting material and α-allyl ketone, respectively.

The synthesis of pentacyclic intermediate **16** in only six steps from 3-acetylindole in good overall yield nicely establishes our route to complex indole alkaloids. The intramolecular Diels–Alder/enol silyl ether alkylation strategy has not previously been employed for the synthesis of indole alkaloids. It offers attractive advantages over alternative routes to this subunit. Efforts to complete the heptacyclic system are in progress.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. H:EA refers to hexanes:ethyl acetate solvent mixtures for TLC and chromatography.

2-(*N*-(1-oxo-4-pentenyl)-3-indolyl)ethanone. To a stirred suspension of 3-acetylindole (3.18 g, 20 mmol) and triethylamine (4.03 g, 40 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added a solution of 4-pentenoyl chloride (2.24 g, 19 mmol) in 25 mL of CH_2Cl_2 over 1 h. The solution was stirred at 0 °C for 8 h and then washed twice with ice-cold 2 N HCl, once with 2 N Na_2CO_3, and once with brine. The organic layer was then dried, concentrated in vacuo, and purified by silica gel flash chromatography (30% ethyl acetate in hexanes) to afford a 79% yield of product. NMR ($CDCl_3$): δ 2.58 (s, 3 H), 2.55–2.7 (m, 2 H), 3.07–3.16 (m, 2 H), 5.08–5.24 (m, 2 H), 5.87–6.02 (m, 1 H), 7.35–7.48 (m, 2 H), 8.12 (s, 1 H), 8.32–8.46 (m, 2 H): IR (CH_2Cl_2): 1718, 1662, 1190, 1115 cm^{-1}. MS: *m/e* 55, 144, 159, 241. HRMS: *m/e* for $C_{15}H_{15}NO_2$ calcd 241.1103, measured 241.1103.

6-((Trimethylsilyl)oxy)-1-oxo-2,3,3a,4,5,7a-hexahydropyrido[3,2,1-*jk*]carbazole (2). To a solution of the N-acylated indole (2.00 g, 8.3 mmol) and diisopropylethylamine (1.78 g, 13.78 mmol) in 40 mL of CH_2Cl_2 at 0 °C was added trimethylsilyltriflate (2.213 g, 9.95 mmol) over 5 min. The solution was stirred at 0 °C for 4 h and then allowed to warm to ambient temperature overnight. The solution was diluted with 250 mL of dry hexanes and was stirred for 5 min. The mixture was filtered, and the filtrate was concentrated in vacuo. Hexanes was again added, and the mixture was filtered and concentrated. This procedure was repeated until a clear oil was obtained. This clear oil was taken on immediately to the next reaction.

The oil was dissolved in 30 mL of dry toluene. To this solution was added hexamethyldisilazane (0.5 mL). The solution was degassed with nitrogen. The tube (Lab Glass Co. – LG9375-104) was closed and heated at 270 °C for 48 h. The tube was cooled.

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The toluene was removed in vacuo. The residue was purified by silica gel flash chromatography (35% ethyl acetate in hexanes) to afford 1.3 g of pure **2**. Compound **2** was a white solid with mp 98–100 °C. NMR ($CDCl_3$): δ 0.28 (s, 9 H), 1.50–2.1 (m, 4 H), 2.40–2.48 (m, 2 H), 2.52–2.80 (m, 2 H), 4.26 (dt, J = 3.2, 9.7 Hz, 1 H), 7.04 (t, J = 7.5 Hz, 1 H), 7.15 (t, J = 7.7 Hz, 1 H), 7.51 (d, J = 7.45 Hz, 1 H), 8.05 (d, J = 7.8 Hz, 1 H). MS: m/e 73, 168, 184, 224, 239, 285, 312, 313. HRMS: m/e for $C_{18}H_{23}NSiO_2$ calcd 313.14981, measured 313.14907. Anal. Calcd: C, 68.97; H, 7.39. Found: C, 68.52; H, 7.39.

1,6-Dioxo-6a-(3,3-diphenyl-2-propenyl)-2,3,3a,4,5,6,6a,7a-octahydropyrido[3,2,1-*jk*]carbazole (6). To a solution of **2** (1.01 g, 3.23 mmol) and alcohol **12** (1.43 g, 6.8 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added $TiCl_4$ (1.82 g, 9.6 mmol) over 3 min. The solution was stirred at −78 °C for 6 h. It was quenched at −78 °C with H_2O (30 mL). Methylene chloride was added, and the organic layer was washed twice with brine, dried, and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (40% ethyl acetate in hexanes) to afford an 80% yield of **6**. Compound **6** was a solid with mp 174–175 °C. NMR ($CDCl_3$): δ 8.11 (d, J = 8 Hz, 1 H), 7.49 (dd, J = 1, 8 Hz, 1 H), 6.95–7.45 (m, 12 H), 5.70 (dd, J = 7.3, 7.9 Hz, 1 H), 3.83 (d, J = 10.1 Hz, 1 H), 2.25–2.85 (m, 6 H), 2.00–2.10 (m, 1 H), 1.80–1.95 (m, 2 H), 1.35–1.65 (m, 2 H). IR ($CDCl_3$): 1720, 1660, 1595, 1490, 1480, 1400 cm^{-1}. MS: m/e 55, 91, 115, 130, 156, 178, 193, 240. HRMS: m/e for $C_{30}H_{27}O_2N$ calcd 433.20419, measured 433.20377. ^{13}C NMR ($CDCl_3$): δ 208.67, 169.52, 146.19, 141.66, 141.15, 139.17, 129.86, 129.60, 128.87, 128.36, 128.10, 127.42, 127.08, 125.59, 124.00, 122.04, 115.60, 67.60, 59.16, 40.89, 37.80, 37.64, 31.23, 25.47, 23.93. TLC (1:1 H:EA): R_f = 0.29.

1,6-Dioxo-6a-(3-oxopropyl)-2,3,3a,4,5,6,6a,7a-octahydropyrido[3,2,1-*jk*]carbazole (13). To a solution of **6** (0.80 g, 1.85 mmol) in CH_2Cl_2 (50 mL) at −78 °C was introduced ozone until the solution turned light blue. The ozone stream was removed and nitrogen was bubbled through the solution. Triphenylphosphine (0.53 g, 2.04 mmol) was added, and the solution was allowed to slowly warm to ambient temperature. The solution was concentrated in vacuo. The residue was purified by silica gel flash chromatography (2:3 hexanes–ethyl acetate) to afford 0.38 g (74% yield) of aldehyde **13**. This solid (mp 208–210 °C) had an R_f of 0.24 in a TLC system of 2:3 H:EA. NMR ($CDCl_3$): δ 9.59 (s, 1 H), 8.10 (d, J = 8 Hz, 1 H), 7.23–7.33 (m, 2 H), 7.06 (dt, J = 0.7, 7.4 Hz, 1 H), 3.77 (d, J = 10.5 Hz, 1 H), 3.57 (d, J = 19 Hz, 1 H), 2.87 (d, J = 19, 1 H), 2.45–2.78 (m, 3 H), 1.85–2.40 (m, 4 H), 1.50–1.80 (m, 2 H). IR ($CDCl_3$) 1720, 1700, 1670, 1590, 1485, 1385 cm^{-1}. MS: m/e 130, 170, 184, 198, 226, 240, 254. HRMS: m/e for $C_{17}H_{17}O_3N$ calcd 283.12085, measured 283.12048. ^{13}C NMR ($CDCl_3$): δ 207.76, 199.44, 172.53, 140.74, 129.49, 129.41, 124.25, 123.57, 116.24, 68.96, 56.60, 54.31, 39.31, 38.47, 31.39, 24.88, 24.78. Anal. Calcd: C, 72.06; H, 6.05. Found; C, 71.90; H, 6.14.

Methyl 1,6-Dioxo-2,3,3a,4,5,6,6a,7a-octahydropyrido[3,2,1-*jk*]carbazole-6a-acetate (14). To a solution of aldehyde **13** (0.30 g, 1.06 mmol) in *t*-BuOH (10 mL) was added 4 mL of a 1.25 M KH_2PO_4 solution followed by 6 mL of a 1 M solution of $KMnO_4$. This was stirred 15 min, and 10 mL of saturated Na_2SO_3 solution was added. The pH of the mixture was adjusted to between 1 and 3 with 2 M HCl. This was extracted with CH_2Cl_2 (10 × 20 mL), and the organic extracts were concentrated. To the residue was added Et_2O (30 mL), and the solution was extracted with 2 M NaOH (3 × 20 mL). The aqueous layer was acidified (to pH 1) and extracted with CH_2Cl_2 (10 × 10 mL). The organic layer was dried with Na_2SO_4 and concentrated to give 0.27 g (85% yield) of the desired acid. The acid was treated with excess diazomethane in CH_2Cl_2 to provide the methyl ester. The methyl ester was a white solid with mp 193–194 °C. NMR ($CDCl_3$): δ 8.10 (d, J = 8 Hz, 1 H), 7.23–7.32 (m, 2 H), 7.06 (dt, J = 1, 8 Hz, 1 H), 3.95 (d, J = 11 Hz, 1 H), 3.68 (s, 3 H), 3.38 (d, J = 18 Hz, 1 H), 2.57 (d, J = 18 Hz, 1 H), 2.50–2.80 (m, 4 H), 2.22–2.40 (m, 1 H), 1.85–2.20 (m, 3 H), 1.65–1.83 (m, 1 H). IR (CH_2Cl_2) 1725, 1705, 1670, 1590, 1475 cm^{-1}. MS: m/e 313, 285, 269, 256, 240, 226, 212, 198, 184, 170. HRMS: m/e for $C_{18}H_{19}O_4N$ calcd 313.13141, measured 313.13078. ^{13}C NMR ($CDCl_3$) δ 208.12, 172.39, 171.55, 140.58, 129.40, 129.31, 124.04, 123.57, 116.12, 68.78, 55.33, 51.85, 45.73, 39.31, 38.30, 31.32, 24.87. TLC (1:1 H:EA): R_f = 0.35.

1,6-Dioxo-6a-(3-aza-2-oxo-4-phenylbutyl)-2,3,3a,4,5,6,-6a,7a-octahydropyrido[3,2,1-*jk*]carbazole (16). To a solution of trimethylaluminium (0.53 mL of a 2 M solution in hexanes, 1.1 mmol) in benzene (5 mL) at −5 to −10 °C was added benzylamine (0.11 g, 1.0 mmol). This was stirred for 30 min, the cold bath was removed, and the solution was allowed to stir 45 min at 25 °C. To this mixture was added the ester (0.29 g, 0.93 mmol) in benzene (10 mL), and the solution was heated at reflux for 24 h. After the solution was cooled to 25 °C, 10 mL of 1 M HCl was added slowly. The organic and aqueous layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The organic extracts were combined, washed with brine, dried, and concentrated. Purification by column chromatography yielded 0.15 g (42%) of lactam **16**. Lactam **16** was a white solid with mp 135–137 °C. NMR ($CDCl_3$): δ 8.10 (d, J = 8 Hz, 1 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.15–7.45 (m, 6 H), 6.99 (dt, J = 0.7, 7.5 Hz, 1 H), 4.63 (d, J = 15 Hz, 1 H), 4.46 (d, J = 15 Hz, 1 H), 3.66 (s, 1 H), 3.40 (d, J = 10.3 Hz, 1 H), 2.76 (d, J = 16.6 Hz, 1 H), 2.58 (d, J = 16.7 Hz, 1 H), 2.35–2.70 (m, 2 H), 2.05–2.20 (m, 1 H), 1.75–2.00 (m, 3 H), 1.50–1.65 (m, 1 H), 1.35–1.50 (m, 2 H). IR (CH_2Cl_2): 3360 (broad), 3050, 1700, 1675, 1595, 1475, 1460 cm^{-1}. MS: m/e 370, 240, 211, 198, 149, 130, 91. HRMS: m/e for $C_{24}H_{24}O_3N_2$ calcd 388.17870, measured 388.17819. ^{13}C NMR ($CDCl_3$) δ 174.06, 173.05, 141.86, 137.98, 130.34, 128.96, 128.54, 127.97, 127.56, 125.30, 124.30, 116.05, 92.87, 69.80, 52.20, 46.22, 42.73, 36.98, 32.18, 31.22, 25.00, 24.13. TLC (H:EA 1:1) R_f = 0.14.

Registry No. (±)-**2**, 124604-54-2; **4**, 703-80-0; (±)-**5**, 124604-55-3; (±)-**6** (R,R′ = Ph), 124604-56-4; **7**, 503-60-6; **8**, 124604-57-5; (±)-**9**, 124604-58-6; **11**, 24626-27-5; **12**, 3923-51-1; (±)-**13**, 124604-60-0; (±)-**14**, 124604-61-1; (±)-**14** (X = OH), 124604-66-6; (±)-**16**, 124604-63-3; (±)-**18**, 124604-67-7; $ClCO(CH_2)_2CH{=}CH_2$, 39716-58-0; (±)-2-(3,3-diphenyl-2-propenyl)cyclohexanone, 124604-59-7; methyl (±)-3-(3,3-diphenyl-2-propenyl)-4-oxo-1-piperidinecarboxylate, 124604-62-2; 2,6-dimethyl-2-(3,3-diphenyl-2-propenyl)cyclohexanone, 124604-64-4; 1-[*N*-(1-oxo-4-pentenyl)-3-indolyl]ethanone, 124604-65-5.