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Canthine Analogs via Intramolecular Diels-Alder Reactions

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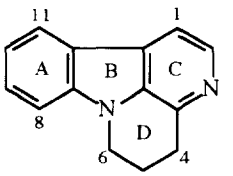
Abstract. - Carbocyclic analogs (**10** and **12**) of canthine (**1**) and canthin-6-one (**2**) were prepared in three and four steps, respectively, from indole-3-carboxaldehyde. The key step was an intramolecular Diels-Alder reaction carried out in refluxing sulfolane.

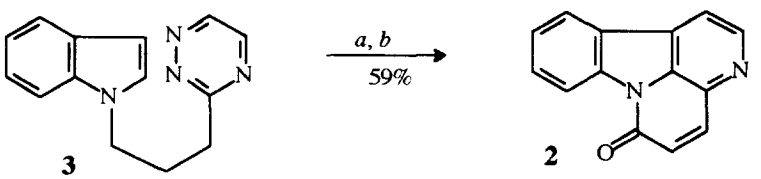
INTRODUCTION

Canthines are tetracyclic β-carboline alkaloids (general structure **1**), several dozen of which have been isolated, characterized, and screened for a wide range of pharmacological activity.[1-3]



1

The preparation of these compounds traditionally has been accomplished by Pictet-Spengler condensations of tryptamine derivatives. Access to various carboline systems has also been gained via Diels-Alder reactions in which indoles functioned as dienophiles.[4] Quite recently Li and Snyder reported a novel intramolecular Diels-Alder pathway to canthin-6-one (**2**) in which the dienophile was C(2)-C(3) of indole and the diene was 1,2,4-triazine tethered to N(1) of indole by a three-carbon chain.[2] Thus **3** afforded **2** upon cycloaddition, nitrogen loss, and subsequent oxidation of intermediate **1** (Scheme 1).



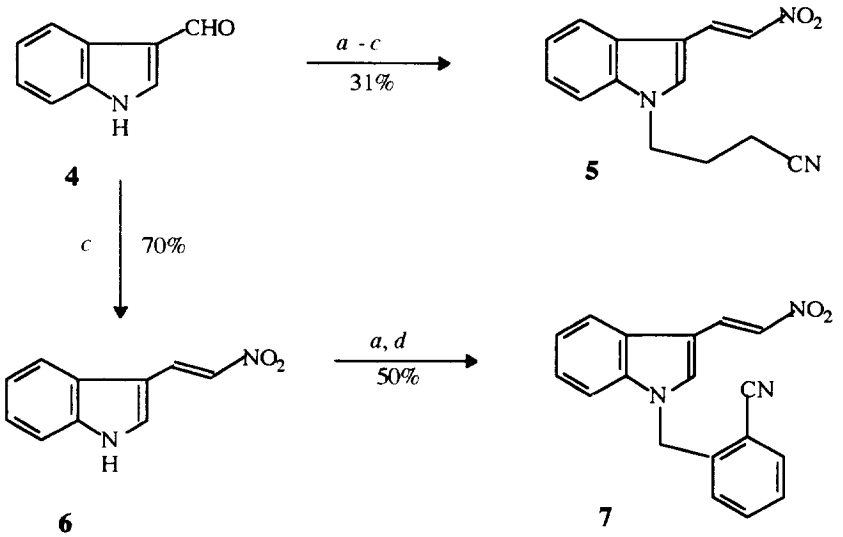
3 **2**

Scheme 1. (*a*) triisopropylbenzene, reflux;
(*b*) $PhCH_2NEt_3^+ MnO_4^-$, CH_2Cl_2, AcOH

Herein we report our investigation of another intramolecular Diels-Alder route to **2**. Our pathway was patterned after prior work that demonstrated 3-vinylindoles function as dienes for inter-[5-8] and intramolecular[9,10] constructions of carbazole and carboline systems. We envisioned a process whereby indole-3-carboxaldehyde (**4**) was converted to 3-(2-nitroethenyl)-1*H*-indole-1-butanenitrile (**5**), suitable for conversion to **2** by thermal cycloaddition, loss of nitrous acid, and oxidation. Nitriles are known dienophiles,[11] and aromatization by HNO_2 loss is well-documented.[5,6,12]

RESULTS AND DISCUSSION

The conversion of **4** to **5** and via **6**[13] to **7** proceeded without difficulty (Scheme 2). The latter compound (**7**) was of interest as a possible precursor of the known benz[4,5]canthin-6-one.[14] Although the NMR spectrum of **6** has been reported,[6d,13be] the chemical shifts of the vinyl protons have not been assigned definitively. In the course of the present work, therefore, we used nitromethane-d_3 to provide **6** labelled at the β-nitrovinyl position, permitting unambiguous attribution of the two vinyl peaks.

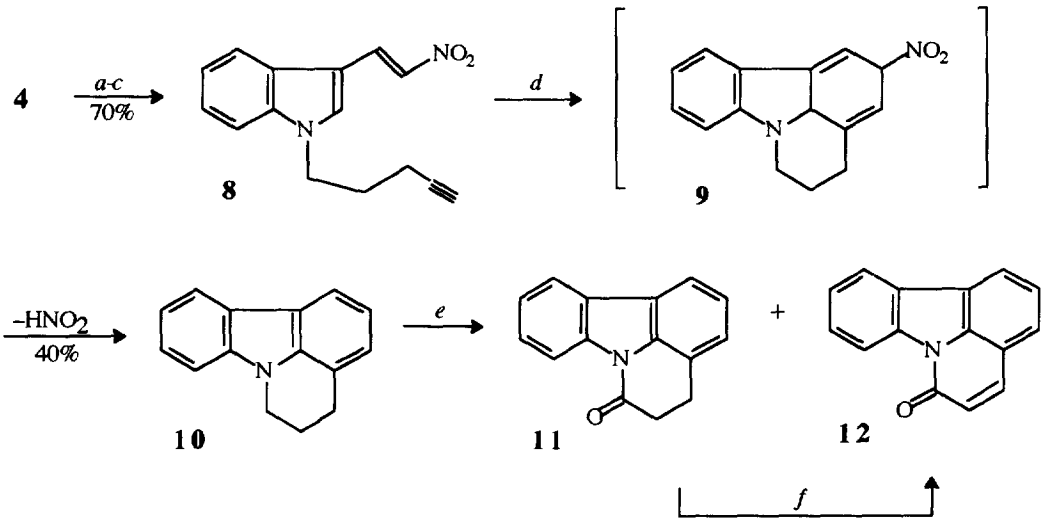


Scheme 2. (*a*) NaH, DMF; (*b*) $BrCH_2CH_2CH_2CN$; (*c*) CH_3NO_2, $AcONH_4$; (*d*) *o*-$BrCH_2C_6H_4CN$.

We anticipated that the Diels-Alder reactions of **5** and **7** would occur at temperatures comparable to those reported by Shimoji (*ca.* 164 °C),[10] Snyder (*ca.* 236 °C),[2a] and Eberle (*ca.* 300 °C).[9] However, we were unable to effect the cycloaddition of either **5** or **7** under conditions involving thermolysis in sulfolane solution at *ca.* 285 °C (1 h reflux) or neat at *ca.* 300 °C (20 min). We turned next to high pressure conditions. The fact that both compounds were recovered unchanged from tetrahydrofuran after four days at 50 °C and 15 kbar was evidence of the low dienophilicity of the cyano group.

At this point attempts to construct the canthine framework were discontinued, and focus was shifted to the carbocyclic analog of canthinone. Thus, **4** was readily converted to **8**, the alkynyl equivalent of **5** (Scheme 3). Probes of the intramolecular Diels-Alder reaction of **8** were carried out in refluxing diglyme, refluxing mesitylene, and toluene (sealed tube, 180 °C) before it was discovered that refluxing sulfolane was the method

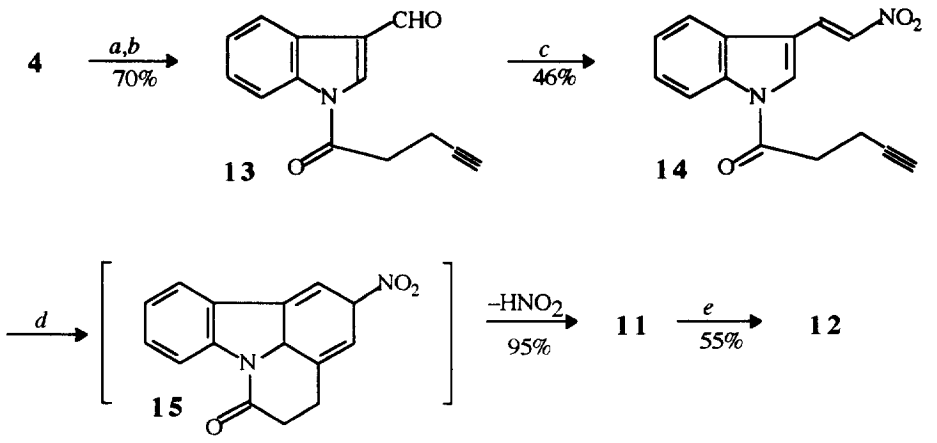
of choice (285 °C, 30 min.). Cycloaddition of **8** thus constructed rings C and D simultaneously, and subsequent loss of HNO_2 from cycloadduct **9** afforded **10**. No product corresponding to aromatization by loss of H_2 from **9** was detected. With 5,6-dihydro-*4H*-pyrido[3,2,1-*jk*]carbazole (**10**) in hand, the final transformation was oxidation of ring D to the enamide. For the analogous conversion of **1** to **2** Li and Snyder used benzyltriethylammonium permanganate (BTAP);[2b] but, mindful of the notorious instability of this compound,[15] we sought to generate it *in situ*. Our modification afforded mixtures of **11** and **12** and, while subsequent treatment with DDQ enhanced the fraction of **12**, the conversion was never complete.



Scheme 3. (*a*) NaH, DMF; (*b*) HC≡CCH$_2$CH$_2$CH$_2$Cl;
(*c*) CH$_3$NO$_2$, AcO NH$_4$; (*d*) sulfolane, Δ;
(*e*) PhCH$_2$NEt$_3$Cl, KMnO$_4$, CH$_2$Cl$_2$, AcOH; (*f*) DDQ, PhMe.

Tetrabutylammonium permanganate,[16] a recommended substitute for BTAP,[15d] was only slightly better as an oxidant; but, even with this reagent, issues of stability remained.[17] At this point our exploratory conversions of **10** to **12** were replaced by a direct route to **11** (*vide infra*). However, the regioselectivity of the permanganate oxidation step remained unresolved. As recognized earlier,[2b] reaction at C(4) in the present case could convert rings C and D into a γ-quinolone moiety. That the structures were, in fact, **11** and **12** was confirmed initially by ^{13}C NMR data and subsequently by the preparation of **11**.

Given our inability to obtain a single product form the oxidation of **10**, we pursued an alternate Diels-Alder route to **11** in which the dienophile was tethered by an amide linkage, analogous to the prior work of Eberle, *et al.*,[9] and Shimoji, *et al.*[10] Accordingly, **4** was converted to **13** and then **14** which, via cycloadduct **15**, afforded **11** (Scheme 4). Oxidation of **11** by DDQ produced **12** more cleanly than the two-step conversion of **10** to **12** (Scheme 3). Thus **10** and **12**, which to our knowledge are the first reported carbocyclic analogs of canthine alkaloids, were prepared in three and four steps, respectively, from **4**.



Scheme 4. (*a*) Et_3N, $HCCl_3$; (*b*) HC≡CCH_2CH_2COCl; (*c*) CH_3NO_2, $AcONH_4$; (*d*) sulfolane, Δ; (*e*) DDQ, PhMe.

EXPERIMENTAL

General Methods. Melting points are uncorrected. IR spectra were recorded in KBr pellets on a Nicolet 550 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). NMR ^1H spectra were obtained on a Brucker WP-200SY spectrometer and ^{13}C spectra were obtained on a Brucker DPX 300 spectrometer; chemical shifts are reported in ppm downfield relative to tetramethylsilane, and coupling constants are reported in hertz (Hz). GC/MS analyses were performed on a Hewlett-Packard 5890II gas chromatograph with an HP-1 crosslinked methyl silicone gum column (12 m x 200 μm with 33 μm film) and a Hewlett-Packard 5791A mass spectrometer (EI, 70 eV). Liquid chromatography (LC) was carried out on short columns of alumina (ICN neutral, Super I, 70-290 mesh) or silica gel (Merck, 35-70 mesh) with elution by dichloromethane. Reaction solutions and solvent extracts were routinely concentrated by rotary evaporation at reduced pressure. Starting materials were obtained from commercial sources and used without further purification. Solvents were dried over molecular sieves. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

3-(2-Nitroethenyl)-1*H*-indole-1-butanenitrile (5). To a stirred suspension of sodium hydride (0.140 g, 60% dispersion in mineral oil, 0.084 g NaH, 3.5 mmol) in dry dimethylformamide (DMF, 1.0 mL) was added dropwise a solution of indole-3-carboxaldehyde (0.453 g, 3.0 mmol) in dry DMF (3.0 mL). After 15 min. a solution of 4-bromobutyronitrile (0.493 g, 3.33 mmol) in dry DMF (1.0 mL) was added and the stirring was continued for 1 h. The reaction mixture was concentrated, and the residual liquid was distributed between CH_2Cl_2 and H_2O; the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined CH_2Cl_2 extract was washed with H_2O (3 x 20 mL), dried ($MgSO_4$), and concentrated to give a dark oil which was treated with ammonium acetate (0.116 g, 1.50 mmol), nitromethane (2.0 mL) and heated at reflux for 45 min., chilled, and suction filtered to give **5** (0.238 g, 31%): mp 126-127 °C; recrystallization from methanol gave the analytical sample: mp 128-129 °C; ^1H NMR (acetone-d_6) δ (multiplicity, area, *J*) 8.35 (d, 1H, 13.5; C*H*=$CHNO_2$), 8.17 (s, 1H; *H*-2), 8.02-7.98 (m, 1H), 7.91 (d, 1H, 13.5; CH=C*H*NO_2), 7.68 (dd, 1H, 6.8,

1.7; *H*-7), 7.39-7.33 (m, 2H), 4.51 (t, 2H, 7.0; NC*H*$_2$), 2.59 (t, 2H, 7.0; C*H*$_2$CN), 2.36-2.29 (m, 2H; C*H*$_2$CH$_2$CN).

Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46.
Found: C, 65.64; H, 4.95; N, 16.32.

3-(2-Nitroethenyl)-1*H*-indole (6). A mixture of indole-3-carboxaldehyde (4.70 g, 32.4 mmol), ammonium acetate (1.0 g, 13 mmol), and nitromethane (20 mL) was heated at reflux for 45 min., chilled, and suction filtered to give **6** (4.28 g, 70.3%), which was recrystallized twice from 95% EtOH: mp 165-167 °C dec. (lit.[6d] mp 169 °C); ^{1}H NMR (DMSO-d_6) δ 12.22 (br s, 1H; N*H*), 8.37 (d, 1H, 13.4; C*H*=CHNO$_2$), 8.19 (s, 1H; *H*-2), 7.96 (d, 1H, 13.4; CH=C*H*NO$_2$), 7.88 (dd, 1H, 6.0, 2.5; *H*-7), 7.48 (dd, 1H, 6.0, 2.2; *H*-4), 7.31-7.19 (m, 2H; *H*-5, *H*-6).

The same procedure at 0.1 scale with nitromethane-d_3 (2.0 mL) gave **5**-d_1: mp 163-166 °C dec. (95% EtOH); IR ν 2325 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.36 (s, 1H; *CH*=CDNO$_2$), 8.19 (s, 1H; *H*-2), 7.91 (dd, 1H, 6.0, 2.5; *H*-7), 7.48 (dd, 1H, 6.0, 2.2; *H*-4), 7.24-7.18 (m, 2H; *H*-5, *H*-6).

2-{[3-Nitroethenyl)-1*H*-indol-1-yl]methyl}benzonitrile (7). To an argon-swept, r.b. flask fitted with a drying tube and containing sodium hydride (0.120 g, 60% dispersion in mineral oil; 0.072 g NaH, 3.0 mmol) was added rapidly a solution of **6** (0.470 g, 2.5 mmol) in dry DMF (12 mL). After the vigorous reaction subsided, to the stirred orange solution was added a solution of 2-(bromomethyl)benzonitrile (0.490 g, 2.5 mmol) in dry DMF (7 mL). The reaction solution was stirred at room temperature for 1 h, diluted with CH_2Cl_2, washed with water (3 x 25 mL), dried ($MgSO_4$), and concentrated to give a dark residual oil which was chromatographed on alumina. From the eluate was isolated a semi-solid residue which was triturated with hot 95% EtOH (70 mL). Concentration of the ethanolic solution gave orange crystals (0.173g; mp 172-175 °C); further concentration gave additional solid (0.069 g; mp 167-170 °C). The insoluble yellow solid (0.161 g) remaining from the trituration was recrystallized from acetone-95% EtOH to give yellow crystals (0.136 g, mp 173-176 °C). The three crops, identical by TLC, were combined (0.378 g, 49.9%), rechromatographed on alumina, and then recrystallized from 95% EtOH to give **7** as yellow crystals (0.187 g): mp 180-181 °C; ^{1}H NMR (acetone-d_6) δ 8.39 (d, 1H, 13.5, C*H*=CHNO$_2$), 8.26 (s, 1H; *H*-2), 8.07-8.03 (m, 1H), 7.95 (d, 1H, 13.5; CH=C*H*NO$_2$), 7.80 (dd, 1H, 7.8, 1.4; *H*-7), 7.70-7.52 (m, 3H), 7.40-7.33 (m, 2H), 7.15 (dd, 1H, 8.5, 1.3), 5.84 (s, 2H; NC*H*$_2$).

Anal. Calcd. for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85.
Found: C, 71.19; H, 4.20; N, 13.73.

1-(4-Pentynyl)-3-(2-nitroethenyl)-1*H*-indole (8). To a stirred suspension of sodium hydride (0.365 g, 60% dispersion in mineral oil; 0.219 g NaH, 9.13 mmol) in dry DMF (5 mL) was added dropwise a solution of **4** (0.879 g, 6.06 mmole) in dry DMF (6 mL), stirring was continued 10 min. at room temperature, and a solution of 5-chloro-1-pentyne (0.819 g, 7.98 mmol) in dry DMF (5 mL) was added rapidly. The reaction mixture was stirred at 70-80 °C for 2 h and concentrated; the residual dark liquid was distributed between CH_2Cl_2 and H_2O, and the aqueous phase was extracted with CH_2Cl_2. The combined CH_2Cl_2 extract was washed with H_2O (3 x 20 mL), dried ($MgSO_4$), and concentrated to give a dark residual oil which was treated with ammonium acetate (0.323 g, 4.19 mmol), nitromethane (6 mL), heated at reflux for 1 h, and then

concentrated. The residual liquid was dissolved in CH_2Cl_2 (75 mL), washed with H_2O (2 x 25 mL), dried ($MgSO_4$), concentrated, and the residual liquid was chromatographed on alumina to give **8** as yellow crystals (1.071 g, 69.5%): mp 85-86 °C; ^1H NMR ($DCCl_3$) δ 8.27 (d, 1H, 13.4; C*H*=CHNO2), 7.78 (dd, 1H, 5.2, 2.3; *H*-7), 7.77 (d, 1H, 13.4; CH=C*H*NO_2), 7.62 (s, 1H; *H*-2), 7.50-7.29 (m, 3H; *H*-4, *H*-5, *H*-6), 4.36 (t, 2H, 6.0; NCH_2), 2.24-2.01 (m, 5H; $CH_2CH_2C{\equiv}CH$).

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02.
Found: C, 70.24; H, 5.72; N, 10.77.

Diels-Alder Reactions of 5, 7, and 8. (A) A solution of **5** (40 mg, 0.16 mmol) in dry tetrahydrofuran (1.0 mL) was filled into a teflon tube and reacted under 15 kbar pressure at 50 °C for 4 d.[18] TLC analysis of the product solution ($HCCl_3$:EtOH, 9:1) showed only recovered starting material (Rf 0.63). Evaporation of the solvent gave a solid whose NMR spectrum was identical to **5**. Similarly, **7** (40 mg, 0.13 mmol) was subjected to the same conditions. TLC and NMR spectral analyses identified the recovered solid as **7** (Rf 0.80). (B) A solution of **8** (0.254 g, 1.0 mmol) in sulfolane (5 mL) was heated at reflux for 1 h. The dark reaction mixture was diluted with Et_2O (25 mL), washed with brine (25 mL), and the aqueous phase was extracted with Et_2O (2 x 20 mL). The combined ether extract was filtered by gravity, washed with brine (5 x 20 mL), dried ($MgSO_4$), and concentrated to give a dark residue (0.261 g), which was chromatographed on alumina (5.4 g). Evaporation of the first eluate fraction gave white solid (0.095 g): mp 73-77 °C; from subsequent fractions was isolated a darker material (0.080 g), which was rechromatographed to give white solid (0.024 g): mp 73-75 °C (from hexane). The combined fraction gave crude **10** (0.119 g, 57.5%). (C) A solution of **8** (0.401 g, 1.58 mmol) in toluene (10 mL) in an argon-swept sealed ampoule was heated at 180 °C for 52 h. The reaction mixture was concentrated, and the dark residual oil (0.373 g) was chromatographed on alumina (5 g). The first two fractions gave a white semi-solid (0.239 g), which was rechromatographed to give crude **10** (0.131 g, 40.2%). Subsequent chromatography on silica gel and then alumina gave crude **10** (0.100 g): mp 66-78 °C, picrate mp 109-111 °C dec.

5,6-Dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole (10). Crude **10** (0.102 g) was dissolved in hot 95% EtOH (4 mL), gravity filtered, and treated with a saturated solution of picric acid in 95% EtOH (3 mL); the reaction solution was concentrated to 5 mL and chilled to give **10**•picrate as purple-red crystals (0.160 g, 74.4%): mp 108-110 °C dec. Recrystallization from 95% EtOH gave the analytical sample: mp 111-112 °C dec.

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 57.80; H, 3.70; N, 12.84.
Found: C, 58.28; H, 3.67; N, 12.39.

The above picrate (0.104 g) was chromatographed on alumina (5 g). Evaporation of the first fraction gave **10** (0.051 g): mp 84-86 °C; ^1H NMR ($DCCl_3$) δ 8.09 (d, 1H, 7.8; *H*-8), 7.89 (dd, 1H, 7.0, 1.6), 7.44-7.32 (m, 2H), 7.24-7.11 (m, 3H), 4.19 (t, 2H, 5.8; *H*-6), 3.05 (t, 2H, 6.1; *H*-4), 2.34-2.22 (m, 2H; *H*-5); ^{13}C NMR (DMSO-d_6) δ 139.4, 137.3, 125.3, 123.0, 122.0, 121.1, 120.7 119.8, 118.6, 118.4, 117.8, 108.9, 40.6, 24,3, 21.9.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76.
Found: C, 86.48; H, 6.31; N, 6.67.

Oxidation of 10 to 11 and 12. (A) To a stirred mixture of **10** (0.0214 g, 0.10 mmol), benzyltriethylammonium chloride (0.0683 g, 0.30 mmol), and powdered potassium permanganate (0.0475 g,

0.30 mmol) in CH_2Cl_2 (2 mL) was added dropwise acetic acid (1 mL); after 5 min. additional acetic acid (4 mL) was added slowly. The reaction mixture was heated at 80-85 °C for 4 h., diluted with ethyl acetate, and concentrated to give a dark residual liquid which was distributed between H_2O (20 mL) and ethyl acetate (40 mL). The biphasic mixture was shaken vigorously, treated with Filter Cel, and suction filtered on a pad of Filter Cel to remove the MnO_2; the aqueous phase of the filtrate was extracted with ethyl acetate. The combined organic phase was washed with H_2O (2 x 10 mL), dried ($MgSO_4$), and concentrated to give a dark residual oil (0.038 g): GC/MS analysis showed two peaks whose *m/z* (M^+) values of 219 and 221 corresponded to ratio of 0.71 for **12:11**. To a solution of the residual oil (0.038 g) in toluene (3.4 mL) was added 2,3-dichloro-3,6-dicyano-1,4-benzoquinone (DDQ; 0.068 g, 0.3 mmol), and the reaction mixture was stirred at reflux for 21 h. The liquid phase was decanted from residual solid, and the latter was triturated with hexane (6 x 4 mL). The combined toluene-hexane phase was filtered by suction and concentrated to give a tan residue (0.045 g): GC/MS analysis showed a ratio of 6.2 for **12:11**. (B) A solution of **10** (0.021 g, 0.10 mmol) and tetrabutylammonium permanganate[17] (0.110 g, 0.30 mmol) in acetic acid (3 mL) was heated at 45-55 °C for 17 h, concentrated, and the residual liquid distributed between H_2O (20 mL) and ethyl acetate (40 mL). The biphasic mixture was worked up as above to give a dark residual oil (0.040 g): GC/MS showed a ratio of 1.4 for **12:11**. A solution of the residual oil (0.040 g) in toluene (3 mL) was treated with DDQ (0.117 g, 0.515 mmole) and stirred at reflux for 24 h. Work up as above gave a red-brown oil (0.061 g): GC/MS showed a ratio of 9.2 for **12:11**. In order that the work-up did not distort initial product ratios, GC/MS analyses were performed on the crude product mixtures. Since these residues contained materials in excess of the theoretical amount of product, percent yields could not be calculated. Products were not isolated.

(1-Oxo-4-pentynyl)-1*H*-indole-3-carboxaldehyde (13). In a 10-mL, r.b. flask fitted with an air condenser and a drying tube a solution of 4-pentynoic acid (1.00 g, 10.2 mmol) in thionyl chloride (1.47 g, 12.3 mmol) was warmed until gas evolution ceased (0.5 h);[19] the cooled reaction mixture was diluted with $HCCl_3$ (20 mL). To a suspension of **4** (1.48 g, 10.2 mmol) in $HCCl_3$ (40 mL)stirred in an ice-bath were added triethylamine (3.0 g, 30 mmol) and the above solution of 4-pentynoyl chloride in $HCCl_3$; stirring was continued at room temperature for 20 h. The reaction solution was washed with 2N HCl (2 x 50 mL), 2N Na_2CO_3 (2 x 50 mL), and H_2O (50 mL), dried ($MgSO_4$), and concentrated to give crude **13** as a tan solid (1.60 g, 69.9%): mp 120-130 °C. Chromatography on silica gel gave **13** (0.815 g, 35.4%): mp 138-139 °C; IR ν 3288, 2126, 1723, 1678 cm^{-1}.

Anal. Calcd. for $C_{14}H_{11}NO_2$: 225.07898
Found (HRMS): 225.07892

3-(2-Nitroethenyl)-1-(1-oxo-4-pentynyl)-1*H*-indole (14). A solution of **13** (0.454 g, 2.02 mmol) and ammonium acetate (0.20 g, 2.6 mmol) in nitromethane (10 mL) was heated at reflux for 1 h and concentrated. The residual oil was dissolved in CH_2Cl_2 (75 mL), washed with H_2O (2 x 25 mL), dried ($MgSO_4$), and concentrated to give a yellow-orange residue which was chromatographed on silica gel to give crude **14** as a yellow solid (0.249 g, 46.4%): mp 152-158 °C. The product was rechromatographed on silica gel to give the analytical sample: mp 166-167 °C; IR ν 2361, 1721 cm^{-1}; ^1H NMR ($DCCl_3$) δ 8.54 (dd, 1H, 6.4, 1.9; *H*-7), 8.19 (d, 1H, 13.7; C*H*=CHNO$_2$), 7.92 (s, 1H; *H*-2), 7.83 (d, 1H, 13.7; CH=C*H*NO$_2$), 7.76

(dd, 1H, 6.3, 2.5; *H*-4), 7.55-7.42 (m, 2H; *H*-5, *H*-6), 3.25 (t, 2H, 7.2; $COCH_2$), 2.78 (td, 2H, 7.2, 2.6; $CH_2C{\equiv}CH$), 2.07 (t, 1H, 2.6; $C{\equiv}CH$).

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44.
Found: C, 66,78; H, 4.68; N, 10.31.

4,5-Dihydro-6*H*-pyrido[3,2,1-*jk*]carbazol-6-one (11). A solution of **14** (0.100 g, 0.37 mmol) in sulfolane (6 mL) was heated at reflux for 10 min., diluted with Et_2O (20 mL), and washed with brine (20 mL); the aqueous phase was extracted with Et_2O (2 x 15 mL). The combined ether extract was washed with brine (5 x 20 mL), dried ($MgSO_4$), and concentrated to give a dark residual oil (0.080 g): GC/MS analysis showed single peak (area > 97%) with *m/z* 221 for **11**. Crude **11** (0.060 g) was chromatographed on alumina (2.5 g) to give a colorless oil (0.028 g) which was dissolved in Et_2O. Slow evaporation of the solvent deposited needles of **11**: mp 53-55 °C; IR ν 1684 cm^{-1}; ^1H NMR ($DCCl_3$) δ 8.50 (d, 1H, 8.1; *H*-8), 7.96 (d, 1H, 7.3), 7.79 (dd, 1H, 6.7, 1.1), 7.55-7.24 (m, 4H), 3.27 (t, 2H, 7.3; *H*-5), 3.03 (t, 2H, 7.3; *H*-4); ^{13}C NMR (DMSO-d_6) δ 167.8, 137.1, 136.7, 127.5, 125.7, 124.6, 124.0, 123.8, 122.7, 121.5, 121.0, 118.3, 115.5, 32.5, 23.5.

Anal. Calcd. for $C_{15}H_{11}NO$: 221.08406
Found (HRMS): 221.08397

6*H*-Pyrido[3,2,1-*jk*]carbazol-6-one (12). To a solution of **11** (0.080 g, 0.36 mmol) in toluene (6 mL) was added DDQ (0.421 g, 1.85 mmol); the reaction mixture was stirred at reflux for 24 h, diluted with hexane (75 mL), and suction filtered. The orange filtrate was concentrated to give a residual red oil: GC/MS analysis showed a major peak (90% area) with *m/z* 219 for **12**. The residual oil was chromatographed on alumina (6 g) to give a red-brown semi-solid (0.067 g, 84%) which was vacuum sublimed twice (1.5 mm Hg, bath temperature 115-135 °C) to give **12** as a pale yellow solid (0.044 g, 55%): mp 123-128 °C. The analytical sample was recrystallized from hexane: mp 133-134 °C; IR ν 1676, 1632, 1605 cm^{-1}; ^1H NMR ($DCCl_3$) δ 8.77 (dd, 1H, 7.5, 0.7; *H*-8), 8.16 (dd, 1H, 7.9, 0.7), 8.10 (dd, 1H, 7.4 1.0), 7.90 (d, 1H, 9.5; *H*-4), 7.73 (dd, 1H, 7.7, 0.6), 7.66-7.46 (m, 3H), 6.48 (d, 1H, 9.5; *H*-5); ^{13}C NMR (DMSO-d_6) δ 159.7, 138.8, 137.9, 128.1, 125.9, 125.5, 125.4, 125.2, 124.3, 124.2, 123.5, 122.8, 121.7, 117.2, 116.2.

Anal. Calcd. for $C_{15}H_9NO$: C, 82.17; H, 4.14; N, 6.38.
Found: C, 81.66; H, 4.22; N, 6.30.

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