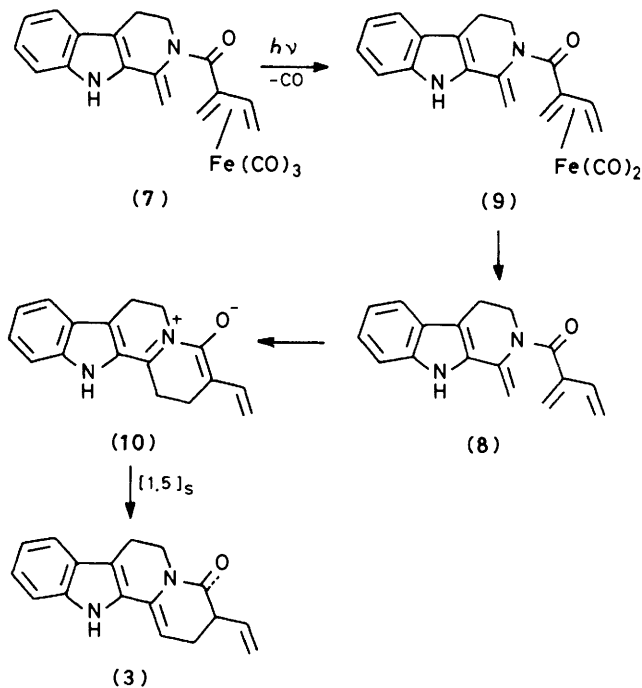


Scheme 2.



Scheme 3.

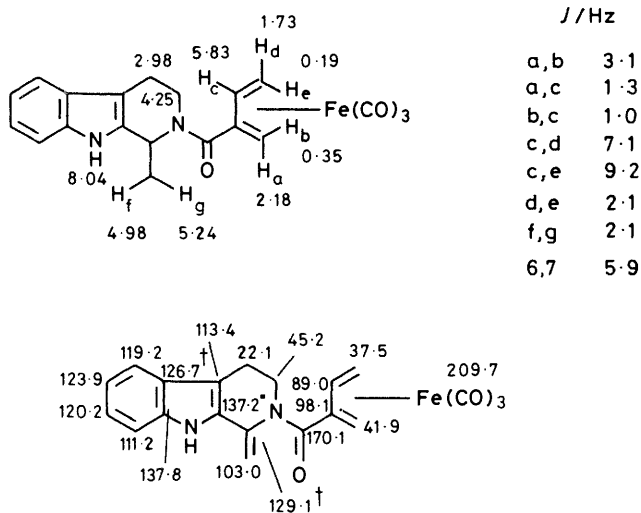


Figure. N.m.r. assignments: chemical shift values with identical superscripts are interchangeable

considerably shielded by virtue of the paramagnetic moment in the metal nucleus.¹⁵ The position and the multiplicity in the single-frequency off-resonance decoupled (SFORD) ¹³C n.m.r. spectrum allowed assignments of all signals. Notably, the specific attribution of the signals due to the two methylene carbons in the diene unit at 37.5 and 41.9 p.p.m. was made possible through the appearance of second-order effects¹⁶ in the off-resonance spectrum (AMX spin system). This may be explained by the fact that the proton chemical shift differences in the two sets of methylene protons are 1.83 and 1.54 p.p.m. (146.4 Hz and 123.2 Hz at 18.7 kG).

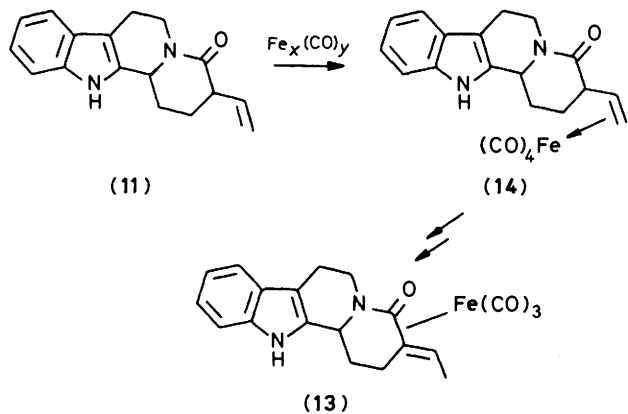
To convert the Fe(CO)₃-enamide (7) into the key compound (3) requires the disengagement of the organic ligand followed by photocyclisation.¹⁷ However the use of oxidants [cerium(IV) ammonium nitrate(CAN),^{18a} iron(III) chloride,^{18b} CAN in

acetone saturated with LiCl,^{18b} manganese dioxide,^{18c} trimethylamine *N*-oxide,^{18d} alkaline 30% hydrogen peroxide^{18e}] for decomplexation of (7) suffers from a plethora of competing reactions. Furthermore, attempts failed to remove the Fe(CO)₃ group from (7) with phosphorus nucleophiles (*e.g.* triphenylphosphine¹⁹), from which only bis(triphenylphosphine)tricarbonyliron²⁰ could be recovered in low yield. We surmise that the major source of difficulty was the propensity of (8) to undergo either overoxidation or hydrolytic ring *C*-fission.²¹

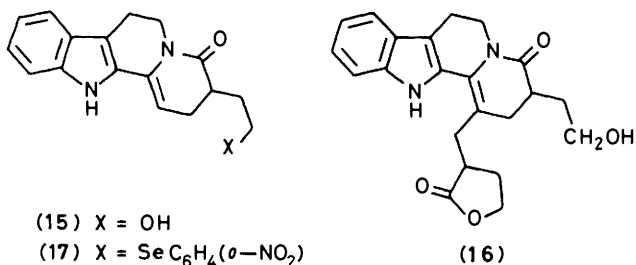
The persistence of these problems led us to consider a procedure which, in principle, would generate (8) photochemically under conditions where its cyclisation would be also favoured. Reports that u.v. irradiation of diene-tricarbonyliron complexes²² gave rise to the corresponding free organic ligand prompted us to investigate this method. Thus, u.v. irradiation through Pyrex of (7) dissolved in pyridine under argon at 0 °C for 30 min gave overwhelmingly the requisite enamide (3) in 76% yield of isolated product. The ¹H n.m.r. spectrum of (3) showed a one-proton triplet (*J* 5.0 Hz) at δ 5.47 for 1-H and three doublets of doublets (first-order analysis) around δ 6.08 (1 H) and 5.18 (2 H) for the vinylic protons.

The formation of (3) presumably involves initial CO dissociation of the η⁴-complex (7) to yield a co-ordinatively unsaturated intermediate (9) which, by subsequent rapid thermal decomposition, gave the uncomplexed diene (8). Hence, the dienamide (8) undergoes a conrotatory 6π-electron electrocyclicisation to generate the dipolar intermediate (10) which, in turn, undergoes a concerted [1,5] suprafacial hydrogen shift to give ultimately (3) (Scheme 3).²³ Remarkably, this tandem excited-state oxidation-cyclisation obviated the isolation and handling of the probably elusive diene (8).

For completion of our scheme, we then examined the reduction of the 1,12b-double bond in (3). This proceeded chemoselectively with activated zinc²⁴ in acetic acid (83%) or under conditions of the Leuckart-Wallach reductive amination (formic acid-dimethylformamide)²⁵ in 72% yield. In both cases, the desired lactam (11) was produced as a 1:1 mixture (by ¹H n.m.r.) of diastereoisomers. However, since the chirality at C-3 is lost in the next step, the mixture was normally used directly. We



Scheme 4.



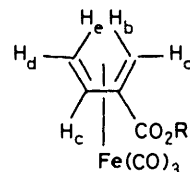
required a stereocontrolled prototropic double bond shift to give the *E*-enamide (12) which would secure the synthesis of the target molecule. Treatment of (11) with a number of reagents expected to lead to (12) was unsuccessful. Thus, use of Bu^tOK,²⁶ rhodium(III) chloride,²⁷ and dichlorotris(triphenylphosphine)ruthenium(II)²⁸ all led to mixtures of *E*- and *Z*-isomers (65–80% yield). The problem was overcome by treating (11) with Fe₂(CO)₉ in dry benzene at 70 °C. Formation of the 'wrong' *Z*-isomer was entirely suppressed and the desired (12) was isolated as the sole product in 77% yield. Although there have been excellent studies²⁹ on the isomerisation of non-conjugated dienes to conjugated systems induced by metal carbonyls, no similar study on the corresponding heterodienes has appeared as yet. No η⁴-heterodiene complex (13)³⁰ has been isolated in the present transformation, but it is presumed to occur as a transient intermediate. As previously invoked for diene isomerisation,³¹ a reasonable pathway to (13) is based on the initial complexation of the C=C double bond to form a η²-Fe(CO)₃ complex (14), followed by intervention of a π-allylhydrotricarbyl complex (Scheme 4). The reason for the high stereoselectivity of the reaction is not completely clear; furthermore it is known that conjugated heterodienes yield only the thermodynamically more stable η⁴-Fe(CO)₃ complex with a *syn-E*-geometry.³²

Finally, construction of the enamide (3) was achieved, albeit in lower overall yields, by a reaction earlier employed by us.⁵ This involved the reaction of the imine (2) with α-methylene-γ-butyrolactone to give (15) in 75% yield after chromatographic purification from the bis-adduct (16). The conversion of (15) into (3) was accomplished by treatment with *o*-nitrophenyl selenocyanate–Buⁿ₃P,³³ followed by oxidative elimination with *m*-chloroperoxybenzoic acid (28% yield) or, more efficiently sodium perborate under phase-transfer catalysis (PTC) conditions³⁴ in 75% yield. Since the enamide (12) has been transformed previously^{2,5} into (±)–(1), the present approaches to (12) complete the formal synthesis of (±)-deplancheine.

Experimental

M.p.s were taken with a hot-stage microscope apparatus. I.r. spectra were recorded for solutions in chloroform unless stated otherwise, with a Perkin-Elmer 681 spectrophotometer. U.v. spectra were recorded for solutions in methanol with a Perkin-Elmer 554 spectrophotometer, and ¹H n.m.r. spectra with a Bruker WP-80 instrument for solutions in CDCl₃ (unless stated otherwise). ¹³C N.m.r. spectra were obtained (CDCl₃) with a Varian XL-100 spectrometer. Chemical shifts are expressed in p.p.m. downfield from internal Me₄Si and coupling constants (*J*) are given in Hertz. Mass spectra were recorded with Varian 112 (model 212 for high-resolution spectra) and CH-7 spectrometers. Compounds were detected on developed chromatograms by fluorescence quenching (245 or 365 nm) and later made visible with cerium(IV) ammonium sulphate (CAS; 1% in 85% phosphoric acid). Flash chromatography was carried out as described by Still³⁵ and performed with silica gel S (Merck; 230–400 mesh).

η⁴-(Ethyl 2-Methylenebut-3-enoate)tricarbyliron (6b).—The procedure of Brion and Martina¹¹ was modified as follows. To a boiling solution of ethyl-2-methylbuta-2,3-dienoate³⁶ (300 mg, 2.38 mmol) in benzene (25 ml), nonacarbonyldi-iron (obtained by a photocustering reaction³⁷) (1.14 g, 3.13 mmol) was added under nitrogen. The initially bright yellow solution turned to deep green. After heating at 70 °C for 10 min, boron trifluoride–ether (193 μl, 15.65 mmol) was added and the resulting solution was heated at reflux for 30 min. After cooling to room temperature and removal of the solvent *in vacuo*, the residue was extracted with *n*-hexane–dichloromethane (3:1) and chromatographed on a silica gel column. The tricarbonyliron(0) complex (6b) appeared as a yellow low-melting solid (316 mg, 50%), *R*_F 0.67 (ethyl acetate–methanol, 95:5); *v*_{max}. 2 060, 1 985, and 1 725 cm⁻¹; δ_H 6.26 (1 H, dddd, *J*_{ce} 9.8, *J*_{cd} 7.2, *J*_{ac} 1.3, *J*_{bc} 1.0 Hz, H_c), 4.35 (2 H, q, *J* 7.0 Hz, OCH₂), 2.43 (1 H, dd, *J*_{ab} 3.0, *J*_{ac} 1.3 Hz, H_a), 1.96 (1 H, dd, *J*_{de} 2.0, *J*_{cd} 7.2 Hz, H_d), 1.30 (3 H, t, *J* 7.0 Hz, CH₃), 0.41 (1 H, dd, *J*_{de} 2.0, *J*_{ce} 9.8 Hz, H_e) and 0.23 (1 H, dd, *J*_{ab} 3.0, *J*_{bc} 1.0 Hz, H_b); *m/z* (150 °C) 266 (*M*⁺, 2%), 238 (37), 210 (81), and 182 (100).



η⁴-(2-Methylenebut-3-enoic Acid)tricarbyliron (6a).—A solution of the foregoing compound (300 mg, 1.26 mmol) in ethanol (50 ml) was cooled at 0 °C and treated with aqueous 0.5M-lithium hydroxide (5 ml). The resulting mixture was stirred under nitrogen for 30 min at 0 °C and overnight at room temperature, and poured into a mixture of brine, ice, and *m*-hydrochloric acid (5 ml). Compound (6a) was extracted with ethyl acetate. The extracts were washed with brine, dried, and evaporated to give pure (6a) (246 mg, 91%) as a pale yellow foam; *R*_F 0.28 (ethyl acetate–methanol, 95:5); *v*_{max}. 2 060, 1 998, and 1 690 cm⁻¹; δ_H 6.30 (1 H, dddd, *J*_{ce} 9.7, *J*_{cd} 7.2, *J*_{ac} 1.3, *J*_{bc} 1.0 Hz, H_c), 3.55 (1 H, br s, CO₂H), 2.43 (1 H, dd, *J*_{ab} 3.0, *J*_{ac} 1.3 Hz, H_a), 2.03 (1 H, dd, *J*_{de} 2.0, *J*_{cd} 7.2 Hz, H_d), 0.50 (1 H, dd, *J*_{de} 2.0, *J*_{ce} 9.5 Hz, H_e), and 0.30 (1 H, dd, *J*_{ab} 3.0, *J*_{bc} 1.0 Hz, H_b).

The Tricarbyliron(0) Enamide (7).—To a solution of 4,9-dihydro-1-methyl-3*H*-pyrido[3,4-*b*]indole (2) (150 mg, 0.815 mmol) in dry dichloromethane (20 ml) was added the complex (6a) (180 mg, 0.75 mmol). The mixture was stirred under

nitrogen for 10 min in an ice bath, and benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP) (367 mg, 0.83 mmol) was added. Stirring was continued at ambient temperature for 20 min. Water was added to the mixture and the organic layer was washed twice with 2N-hydrochloric acid and then with 5% sodium hydrogen carbonate and water. The solvent was removed and the oily residue was purified by silica flash-chromatography (n-hexane-ethyl acetate, 7:3) to afford pure *compound (7)* (255 mg, 84%) as a pale yellow solid; R_F 0.38 (n-hexane-ethyl acetate, 7:3); orange spot (CAS); ν_{\max} . (CCl₄) 3 470, 2 057, 1 994, 1 974, 1 968, and 1 655 cm⁻¹; λ_{\max} . 209, 226sh and 304 nm; m/z (200 °C) 404 (M^+ , 2.5%), 376 (18), 348 (72), 320 (100), 292 (38), 290 (48), 264 (41), 249 (33), 238 (92), 182 (48), and 160 (33).

Photoinduced Decomplexation of the η^4 -Tricarbonyliron Enamide (7) and Cyclisation to 3-Ethenyl-2,6,7,12-tetrahydroindolo[2,3-a]quinolizin-4(3H)-one (3).—Freshly dried and degassed pyridine (15 ml) was transferred *in vacuo* into a Pyrex Schlenk flask (50 ml) charged with (7) (195 mg, 0.482 mmol), and the solution was irradiated under argon (125 W mercury medium-pressure arc fitted with a Pyrex glass filter transmitting > 300 nm). The photolysis was monitored by t.l.c. and continued until this showed no remaining starting material (30 min). The solvent was removed *in vacuo* and the brown residue taken up in dichloromethane (20 ml). This solution was filtered through Celite and washed with 10% phosphoric acid, 10% sodium hydrogen carbonate, and then water. The organic layer was dried over sodium sulphate and the solvent was removed to leave a pale yellow foam (115 mg), which was purified by silica flash-chromatography. Elution with dichloromethane-ethyl acetate (19:1) gave *3-ethenyl-2,6,7,12-tetrahydroindolo[2,3-a]quinolizin-4(3H)-one (3)* (97 mg, 76%), as a colourless solid; R_F 0.25 (dichloromethane-ethyl acetate, 97:3) as an orange spot (CAS); λ_{\max} . 226, 309, and 320 nm; ν_{\max} . 3 470, 1 667, and 1 650 cm⁻¹; δ_H [(CD₃)₂SO] 8.00 (1 H, br s, NH), 6.08 (1 H, ddd, J_1 17.5, J_2 9.7, J_3 6.7 Hz, CH=CH₂), 5.47 (1 H, t, J 5.0 Hz, 1-H), 5.19 (1 H, ddd, J_1 17.5, $J_2=J_3$ 1.4 Hz, =CH₂), 5.18 (1 H, ddd, J_1 9.7, $J_2=J_3=1.4$ Hz, =CH₂), 4.24 (1 H, ddd, $J_{6\alpha,6\beta}$ 13.3, $J_{6\alpha,7\alpha}=J_{6\alpha,7\beta}$ 5.6 Hz, 6 α -H), 3.99 (1 H, ddd, $J_{6\alpha,6\beta}$ 13.3, $J_{6\beta,7\alpha}=J_{6\beta,7\beta}$ 6.2 Hz, 6 β -H), 3.23 (1 H, br t, J 7.0 Hz, 3-H), 2.91 (2 H, dd, $J_{6\alpha,7}$ 5.6, $J_{6\beta,7}$ 6.2 Hz, 7-H), and 2.55 (2 H, m, 2-H) (Found: M^+ 264.1265. Calc. for C₁₇H₁₆N₂O: M^+ , 264.1262).

Chemoselective Reduction of (3) to the Diastereoisomeric 3-Ethenyl-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-ones (11).—To a stirred suspension of activated zinc dust (104 mg, 1.6 g atom) prepared according to the method of Tsuda²⁴ in tetrahydrofuran (15 ml) was added a solution of the enamide (3) (85 mg, 0.32 mmol) in glacial acetic acid (5 ml). The mixture was heated at 50 °C under nitrogen and after 30 min, when the reduction was complete (t.l.c. showed an apparently single more polar spot), the mixture was cooled in an ice bath and treated dropwise with 2M-sodium hydroxide solution. The precipitate was filtered off with suction and thoroughly washed with ethyl acetate. The combined filtrates were washed with water and brine, filtered through anhydrous sodium sulphate, and concentrated under vacuum. The resulting greenish oil was purified by silica flash-chromatography (chloroform-ethyl acetate, 19:1) to give the compound (11) (71 mg, 83%) as a 1:1 mixture of diastereoisomers (checked by ¹H n.m.r.) which was immediately carried forward to the next reaction; ν_{\max} . 3 470, 1 640, and 1 630 cm⁻¹; m/z (150 °C) 266 (M^+ , 100%), 265 (33), 237 (28), 210 (17), 184 (22), and 169 (98) (Found: M^+ , 266.1422. Calc. for C₁₇H₁₈N₂O: M^+ , 266.1419). Diastereoisomer (A) had δ_H 6.19 [ddd, J_1 15.9, J_2 11.3, J_3 1.4 Hz, C(3)-CH=], 5.13 [dt, $J_1=J_2=1.4$, J_3 15.9 Hz, C(3)-C=CH] and 5.16 [dt, $J_1=J_2=1.4$, J_3 11.3 Hz, C(3)-C=CH]. Diastereoisomer (B) had δ_H 6.19 [ddd,

J_1 18.4, J_2 8.9, J_3 1.4 Hz, C(3)-CH=], 5.15 [dt, $J_1=J_2=1.4$, J_3 18.4 Hz, C(3)-C=CH], and 5.21 [dt, $J_1=J_2=1.4$ Hz, J_3 8.9 Hz, C(3)-C=CH].

(E)-3-Ethylidene-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-one (12).—A slurry of compound (11) (65 mg, 0.244 mmol) and nonacarbonyl-di-iron (221 mg, 0.60 mmol) in degassed dry benzene (10 ml) was heated under nitrogen for 30 min at 70 °C; the yellow colour turned to deep green. After cooling to room temperature and removal of the solvent *in vacuo*, the residue was exhaustively extracted with dichloromethane. Concentration followed by preparative t.l.c. (silica gel; chloroform-ethyl acetate, 19:1) gave in the R_F 0.23 band the pure *compound (12)* (49 mg, 77%) as a colourless crystalline solid, m.p. 241 °C (diethyl ether) (lit.² 245 °C) (Found: C, 76.5; H, 6.9; N, 10.5. C₁₇H₁₈N₂O requires C, 76.7; H, 6.8; N, 10.5%); δ_H [(CD₃)₂SO] 1.72 (3 H, d, J 8 Hz, CH₃-C=), 4.86 (1 H, dd, J_1 12, J_2 2 Hz, 12b-H), 4.95 (1 H, dd, J_1 13, J_2 2.5 Hz, 6 α -H), 6.74 (1 H, q, J 8 Hz, CH₃-CH=), 6.95 and 7.05 (2 H, t + t, J 8 Hz, 9-H and 10-H), 7.30 and 7.39 (2 H, d + d, J 8 Hz, 8-H and 11-H), and 10.92 (1 H, br s, NH); m/z (120 °C) 266 (M^+ , 100%), 249 (18), and 235 (27).

3-(1-Hydroxyethyl)-2,6,7,12-tetrahydroindolo[2,3-a]quinolizin-4(3H)-one (15).—To a solution of the imine (2) (1.5 g, 8.1 mmol) in xylene-dimethylformamide (25:1) (80 ml) was added 3-methylene-4,5-dihydrofuran-2(3H)-one (440 μ l, 5.0 mmol) and the mixture was refluxed under nitrogen. More furanone (340 μ l, 3.9 mmol) was added to the solution and the reaction was monitored by t.l.c. After the mixture had been refluxed for 48 h, t.l.c. (ethyl acetate-methanol, 9:1) showed a major component (R_F 0.34) and a minor one (R_F 0.21). The solvent was distilled off and the residue was taken up in ethyl acetate and extracted three times with M-hydrochloric acid. The organic phase was washed with brine, dried, and evaporated to give a yellow-orange crystalline residue (2.2 g) which was separated by flash-chromatography. On elution with ethyl acetate-methanol (19:1), the first fractions afforded *compound (15)* (1.71 g, 75%), m.p. 208 °C (methanol) (Found: C, 72.2; H, 6.5; N, 9.9. C₁₇H₁₈N₂O₂ requires C, 72.3; H, 6.4; N, 9.9%); λ_{\max} . 231, 309, and 321 nm; δ_H [(CD₃)₂SO] 1.56–2.74 (5 H, m, 2-H + 3-H + CH₂OH), 2.88 (2 H, dd, J_1 6, J_2 5 Hz, 7-H), 3.66 (1 H, dt, J_1 12, J_2 5 Hz, 6-H), 4.16 (1 H, t, J 6 Hz, OH), 4.32 (1 H, dt, J_1 12, J_2 5 Hz, 6-H), and 5.74 (1 H, t, J 5 Hz, 1-H); m/z (120 °C) 282 (M^+ , 49%), 238 (78), 237 (36), and 210 (100). Evaporation of later fractions from the column afforded the γ -lactone (16) (245 mg, 8%) as pale yellow foam; λ_{\max} . 230, 310, and 321 nm; ν_{\max} . 3 340, 1 753, and 1 630 cm⁻¹; δ_H [(CD₃)₂SO] 2.90 (2 H, br t, J 5.5 Hz, 7-H), 3.48 (1 H, dt, J_1 15, J_2 2.5 Hz, 6 β -H), 3.76 (2 H, br t, J 5 Hz, CH₂OH), 4.34 (2 H, ddd, J_1 10, J_2 6, J_3 5 Hz, CH₂-OCO), and 9.76 (1 H, br s, NH); m/z (150 °C) 380 (M^+ , 25%), 335 (33), 295 (100), 282 (26), 238 (43), and 210 (46).

3-[2-(2-Nitrophenylseleno)ethyl]-2,6,7,12-tetrahydropyridindolo[2,3-a]quinolizin-4(3H)-one (17).—To a solution of (15) (550 mg, 1.95 mmol) and sublimed 2-nitrophenyl selenocyanate (475 mg, 2.10 mmol) in tetrahydrofuran-pyridine (1:1) (15 ml) was added tri-n-butylphosphine (515 μ l, 2.10 mmol) at ambient temperature. After stirring for 3 h under nitrogen, the solvent was evaporated off and the *selenide (17)* (455 mg, 50%) was isolated after flash-chromatography (dichloromethane-ethyl acetate, 49:1) as a yellow solid, R_F 0.34 (orange spot with CAS); δ_H [(CD₃)₂SO] 11.14 (1 H, br s, NH), 8.25 (1 H, dd, J_1 7.8, J_2 1.8 Hz, 3'-H), 5.86 (1 H, br t, J 4.8 Hz, 1-H), and 4.38 (1 H, dt, J_1 12.4, J_2 4.7 Hz, 6 α -H); m/z (200 °C) 467 (M^+ , 5%), 281 (100), 265 (28), and 263 (38).

3-Ethenyl-2,6,7,12-tetrahydroindolo[2,3-a]quinolizin-4(3H)-one (3) from the Selenide (17).—To a cooled (0 °C) stirred

solution of the selenide (17) (235 mg, 0.50 mmol) in dichloromethane-acetic acid (19:1) (25 ml) under nitrogen were added tetrabutylammonium hydrogen sulphate (18 mg, 0.055 mmol) and then portionwise sodium perborate tetrahydrate (85 mg, 0.55 mmol). After being stirred for 1 h at 0 °C, the solution was poured onto ice. The resulting organic phase was washed with saturated sodium hydrogen carbonate solution and dried (sodium sulphate). Concentration *in vacuo*, followed by preparative t.l.c. (chloroform-ethyl acetate, 19:1), gave compound (3) (100 mg, 75%), identical with that obtained by decomplexation-cyclisation of the η^4 -tricarbonyliron(0) complex (7).

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Received 12th December 1983; Paper 3/2189