Pergamon

Tetrahedron Vol. 51, No. 1, pp. 59-66, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00963-5

Porphyrins with Exocyclic Rings. Part 5.[1]
Synthesis of a Naphtho[1,2-b]porphyrin.[2]

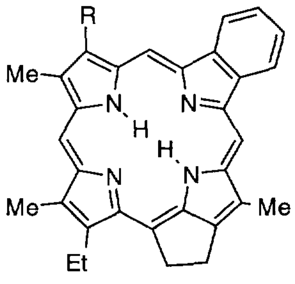
Timothy D. Lash* and Carl P. Denny

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, U.S.A.

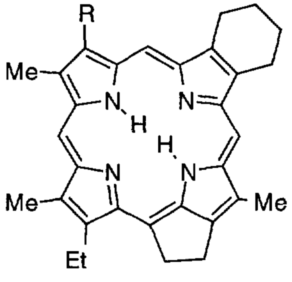
Abstract: *Condensation of 2-acetyl-1-tetralone with diethyl aminomalonate in refluxing acetic acid gave a dihydronaphthopyrrole* ***9a*** *in excellent yield. Transesterification with benzyl alcohol gave the corresponding benzyl ester* ***9b*** *and subsequent regioselective oxidation with lead tetraacetate afforded the acetoxymethyl derivative* ***13****. Pyrrole* ***13*** *condensed with the α-unsubstituted pyrrole* ***14*** *to give the asymmetrical dipyrrylmethane* ***15*** *and hydrogenolysis over 10% palladium-charcoal yielded the related dicarboxylic acid* ***16****. Acid catalyzed condensation of* ***16*** *with dipyrrylmethane dialdehyde* ***18*** *gave the dihydronaphthoporphyrin* ***17*** *in 44% yield. Alternatively,* ***17*** *condensed with two equivalents of pyrrole aldehyde* ***19*** *in the presence of HBr to give the a,c-biladiene* ***20*** *and cyclization with $CuCl_2$ in DMF, followed by demetallation with 10% H_2SO_4 in TFA, afforded* ***17*** *in 37% yield. Dehydrogenation of* ***17*** *with DDQ in refluxing toluene gave* ***8****, the first example of a naphthoporphyrin, in 76% yield. Porphyrin* ***8*** *exhibited an unusual electronic spectrum and this may have value in the characterization of sedimentary porphyrins.*

INTRODUCTION

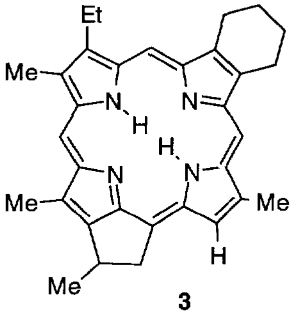
The presence of a minor group of petroporphyrins with electronic spectra resembling the so-called rhodoporphyrins in oil shales and petroleum was first recognized in the early 1960's.[3,4] Mass spectrometric and infrared data indicated that these "rhodoporphyrins" were in actuality monobenzoporphyrins.[4] Subsequently, synthetic monobenzoporphyrins were shown to have similar spectroscopic properties to these sedimentary compounds.[5,6] Recently, a number of benzoporphyrins (e.g., **1**) and tetrahydrobenzoporphyrins (e.g., **2** and **3**) have been isolated and characterized from organic-rich sediments,[7,8] but there is no concensus on the origins of these materials.[6-9] The presence of a five-membered exocyclic ring in these structures strongly suggests that they were formed from chlorophyll precursors but no known biologically significant tetrapyrrolic pigments incorporate a structural unit that could conceivably give rise to the benzo moiety.



1 a. R = Et
b. R = Me

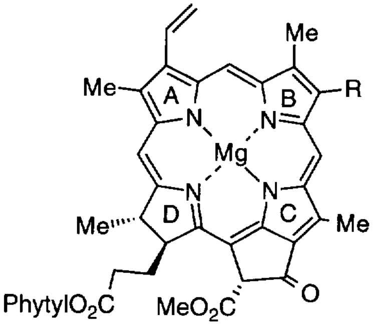


2 a. R = Et
b. R = Me



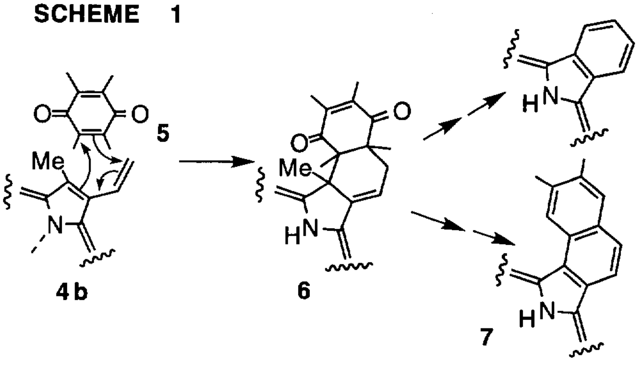
3

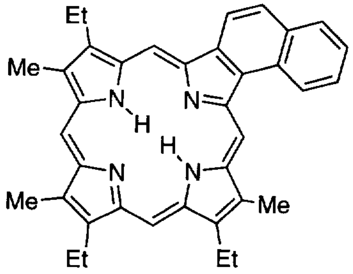
A plausible pathway for the formation of these unusual molecular fossils involves the Diels-Alder cycloaddition of a plastoquinone **4** with a divinylchlorophyll **5b** to give the adduct **6** (Scheme 1), followed by further degradation and aromatization.[6a,9] Plastoquinones are present as major constituents of photosynthetic organisms. In addition, Diels-Alder cycloaddition reactions between various dienophiles and vinylporphyrins have been studied in detail[10] and these studies provide indirect evidence for this hypothesis. Chlorophyll-a (**5a**) could not give rise to petroporphyrins **1** and **2**, since the vinyl grouping is placed on the "A" ring, whereas the benzo- or tetrahydrobenzo- ring fusion in the geological compounds lie on the B ring. However, divinyl chlorophyll-a (**5b**) is commonly found in marine algae[11] and it has been argued that cycloadditior reactions would occur regioselectively at the B ring due to the formation of the relatively favored bacteriochlorin chromophore.[6b] If this proposal for the formation of sedimentary benzoporphyrins is indeed correct, it seems likely that naphtho[1,2-b]porphyrins **7** could also be formed from the early intermediate **6** (Scheme 1). The presence of porphyrins fused to extended benzenoid aromatic systems in mature sediments has been postulated[12] but little direct evidence for these species have been forthcoming. Naphtho[1,2-b]porphyrins had not been investigated previously and their spectroscopic properties were unknown. Hence, we set out to synthesize the first example of a naphthoporphyrin (**8**) and the results of these studies are shown below.



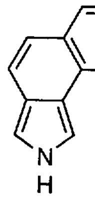
4 a. R = Et (Chlorophyll-a)
b. R = $CH{=}CH_2$

SCHEME 1





8

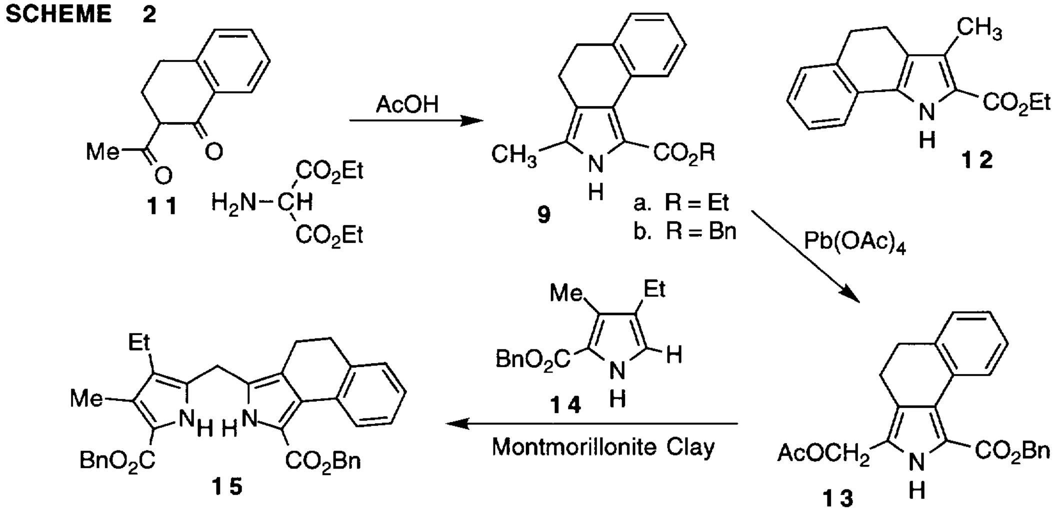


10

RESULTS AND DISCUSSION

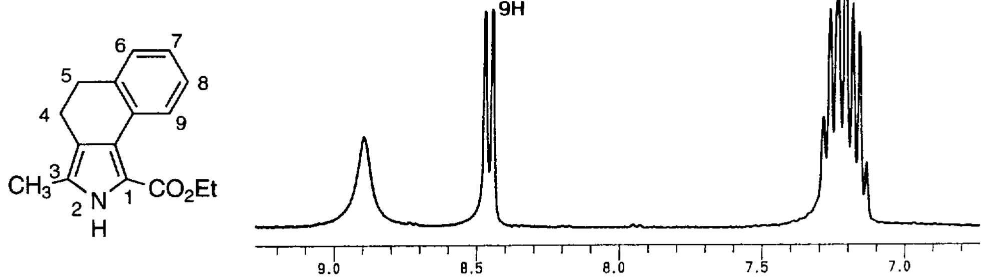
We have previously reported the synthesis of structurally diverse cycloalkanoporphyrins[1,13-18] from cycloalkenopyrroles. In line with these earlier studies, we speculated that the naphtho[1,2-b]porphyrin system could be built up from the dihydronaphthopyrrole **9** (Scheme 2). The fully conjugated naphtho[1,2-c]pyrroles **10** were likely to be less suitable for these studies, as they structurally resemble the relatively unstable isoindoles and such a system would no doubt exhibit quite different chemistry from substituted pyrroles such as **9**. Nonetheless, such a strategy necessitates an oxidation step at a late stage in the synthesis to form the naphtho subunit. Although this transformation could be potentially problematical, we anticipated that this dehydrogenation would be a facile process.

SCHEME 2



Dihydronaphthopyrrole **9a** has been previously prepared in moderate yield from ethyl glycinate.[19] In our work, we achieved substantially improved yields of **9a** by reacting 2-acetyl-1-tetralone (**11**) with diethyl aminomalonate[16,20] in refluxing acetic acid (Scheme 2). In principle, condensation of diethyl aminomalonate with **11** might yield **9a** or the isomeric dihydronaphtho[1,2-b]pyrrole **12**. However, only dihydronaphthopyrrole **9a** appeared to be formed in our studies and no trace of **12** was detected. This is perhaps not surprising, since the initial site of nucleophilic attack is likely to be the acetyl unit of **11** rather than the ring carbonyl (Scheme 2). Initial reaction would have to occur at the latter site in order for **12** to be formed. The structure assignment of the product was based upon the mp and proton NMR spectrum (Fig. 1). The resonance due to the 9-H of **9a** was particularly deshielded due to its proximity to the carbonyl unit and appears at 8.45 ppm. None of the aromatic protons in **12** would be expected to be shifted downfield to this extent.

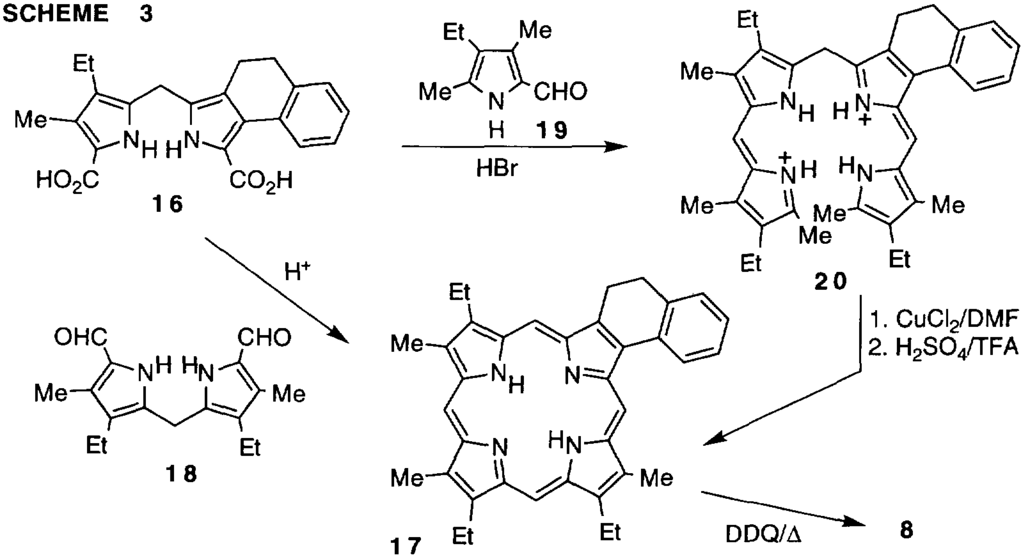
Figure 1: Partial 300 MHz Proton NMR Spectrum for **9a** in deuteriochloroform.



Base catalyzed transesterification of **9a** with benzyl alcohol gave the corresponding benzyl ester **9b** in 87% yield. Reaction with lead tetraacetate in glacial acetic acid afforded the acetoxymethylpyrrole **13** and subsequent reaction with α-unsubstituted pyrrole **14**[18,21] in the presence of Montmorillonite clay[22] then gave the dipyrrylmethane **15** in good yield (Scheme 2). Hydrogenolysis of **15** over 10% palladium-charcoal removed the protective benzyl esters to give the dicarboxylic acid **16** (Scheme 3). This key intermediate was then converted into the dihydronaphthoporphyrin **17** by two different methods (Scheme 3).

The MacDonald condensation[23] gave **17** in a single step from **16** and diformyldipyrrylmethane **18**. Hence, condensation of dipyrrylmethane **16** with **18** in the presence of p-toluenesulfonic acid in methanol/dichloromethane, followed by air oxidation in the presence of zinc acetate, gave the dihydronaphthoporphyrin **17** in 44% yield. Alternatively, dipyrrylmethane **16** could be condensed with two equivalents of pyrrole aldehyde **19** in the presence of hydrobromic acid to give the a,c-biladiene dihydrobromide salt **20**. Copper(II) chloride mediated cyclization[24] of **20**, followed by demetallation with 10% sulfuric acid-trifluoroacetic acid afforded porphyrin **17** in 37% yield. Originally it had been speculated that further oxidation to **8** might occur under the cyclization conditions, but this was not observed in these studies.

SCHEME 3



Porphyrin **17** was dehydrogenated with DDQ in refluxing toluene, and following chromatography and crystallization from dichloromethane-methanol naphthoporphyrin **8** was isolated in 76% yield. Naphthoporphyrin **8** showed a characteristic proton NMR spectrum (Fig. 2), where one of the *meso*-bridge resonances had been shifted to approximately 11 ppm due to its proximity to the naphtho unit. The uv-vis spectrum of **8** was also distinctive, and this may prove to be of value in detecting naphthoporphyrins in sedimentary materials. The Soret band was slightly red shifted and appeared at an unremarkable 415 nm. The less intense Q bands in the visible region (Fig. 3) also underwent a small bathochromic shift relative to the spectra observed for simple monobenzoporphyrins. However, the relative intensities of these absorptions were particularly diagnostic, showing a prominent band III and a relatively small band I. Further synthetic studies on related systems are underway and these results may provide a better understanding of the observed shifts in the electronic spectra of conjugated porphyrins.

CONCLUSIONS

Dihydronaphthopyrroles **9** have been prepared in high yields by condensing 2-acetyl-1-tetralone with diethyl aminomalonate. Using conventional methodologies, these intermediates were converted into the novel dihydronaphthoporphyrin **17** via the MacDonald condensation and the a,c-biladiene approach.

Dehydrogenation of **17** with DDQ in refluxing toluene afforded the first example of a naphtho[1,2-b]porphyrin (**8**), and this compound exhibited an unusual electronic spectrum that may have value in the detection of porphyrin molecular fossils. The chemistry described in this paper is reasonably versatile and may potentially be applicable to the synthesis of related systems. Further studies on the synthesis of porphyrins fused to extended aromatic systems are currently underway.[25]

Figure 2: Partial 300 MHz proton NMR spectrum of naphthoporphyrin **8** in $CDCl_3$.

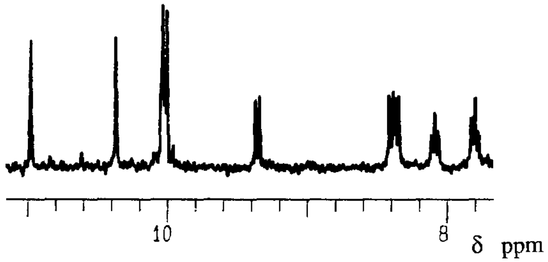
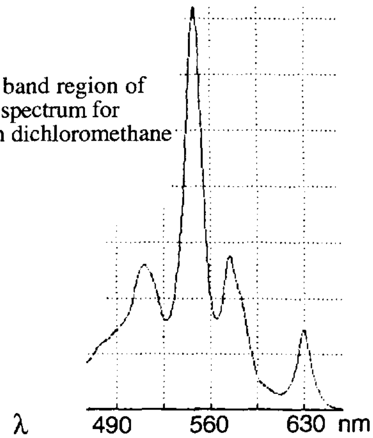


Figure 3: Q band region of the electronic spectrum for porphyrin **8** in dichloromethane



EXPERIMENTAL

2-Acetyl-1-tetralone, lead tetraacetate, Montmorillonite clay, DDQ and 30% hydrogen bromide in acetic acid were purchased from the Aldrich Chemical Co. and were used without further purification. Porphyrins were chromatographed on Grade 3 alumina or silica (deactivated with 10 mL of water per 100 g silica). Hydrogenations were carried out in a Parr hydrogenator at 40 psi. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 710B spectrometer or a Perkin-Elmer 1600 Series FT-IR Spectrometer, and UV-vis spectra were obtained on a Beckmann DU-40 spectrophotometer. NMR spectra were recorded on a Hitachi-Perkin Elmer R24B 60 MHz nmr spectrometer or a Varian Gemini-300 nmr spectrometer. Mass spectral determinations were made at the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). Elemental analyses were obtained from Micro-Analysis, Inc., Wilmington, DE 19808.

Ethyl 4,5-Dihydro-3-methylnaphtho[1,2-c]pyrrole-1-carboxylate (9a). Diethyl aminomalonate (**3** ; 43.70 g) was added dropwise over a period of 5 min to a refluxing solution of 2-acetyl-1-tetralone (25.00 g) in acetic acid. The mixture was refluxed for a further 1 hr, cooled to 70°C and poured into ice/water (1000 mL). The resulting precipitate was filtered, washed with water and recrystallized from 95% ethanol to give pyrrole **9a** (29.49g; 78%) as off-white crystals, mp 144-145°C (lit. mp[19] 144.5-147°C). IR (Nujol mull): ν 3307 (NH str.), 1652 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.39 (3H, t, J = 7 Hz, CH_2CH_3), 2.24 (3H, s, pyrrole-CH_3), 2.54 (2H, t, J = 7 Hz), 2.84 (2H, t, J = 7 Hz) (CH_2CH_2), 4.36 (2H, q, J = 7 Hz, OCH_2), 7.20 (3H, m, 6, 7 and 8-H), 8.45 (1H, d, J = 7.7 Hz, 9-H), 8.89 (1H, br, NH); ^{13}C NMR ($CDCl_3$): δ 11.21, 14.58, 19.98, 31.09, 60.26, 115.15, 120.87, 126.37, 126.74, 127.19, 127.61, 127.97, 131.12, 137.54, 161.03.

Benzyl 4,5-Dihydro-3-methylnaphtho[1,2-c]pyrrole-1-carboxylate (9b). A solution of foregoing dihydronaphthopyrrole **9a** (5.00 g) in benzyl alcohol (12 ml) was placed in a 100 mL Erlenmeyer flask and heated with stirring on an oil bath. A solution of sodium benzyloxide was prepared by dissolving sodium (0.5 g) in benzyl alcohol (10 mL). Approximately 0.5 mL of the sodium benzyloxide solution was added to the solution and the temperature of the oil bath was allowed to slowly rise from room temperature to 230°C over a period of 90 min, while small portions of sodium benzyloxide solution (total of 3-4 mL) were added periodically to the reaction mixture. Early on in the procedure, a thermometer placed in the neck of the flask detected vapors at 70-90°C. When the temperature of the vapors at the neck of the flask reached 200°C, one further portion of sodium benzyloxide was added and the mixture was stirred for 5 min. The hot solution was poured into a stirred mixture of methanol (30 mL), water (22 mL) and acetic acid (0.5 mL). The mixture was cooled in an ice bath, and the resulting precipitate filtered and washed well with water. Recrystallization from ethanol gave the benzyl ester **9b** (5.41 g; 87%) as shiny white crystals, mp 140.5-141.5°C; IR (nujol mull):

v 3309 (NH str.), 1645 (C=O str.) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.19 (3H, s, pyrrole-CH_3), 2.52 (2H, t, J = 7 Hz), 2.82 (2H, t, J = 7 Hz) (CH_2CH_2), 5.32 (2H, s, OCH_2), 7.1-7.24 (3H, m, 6, 7 and 8-H), 7.3-7.45 (5H, m, Ph), 8.45 (1H, m, 9-H), 8.87 (1H, br, NH); ^{13}C NMR ($CDCl_3$): δ 11.10, 19.87, 30.95, 65.98, 114.64, 120.92, 126.36, 126.75, 127.50, 127.63, 127.86, 128.22, 128.54, 130.89, 136.21, 137.49, 160.52.

Anal. calc. for $C_{21}H_{19}NO_2$: C, 79.46; H, 6.04; H, 4.41. Found: 79.06; H, 6.17; N, 4.46.

Benzyl 3-Acetoxymethyl-4,5-dihydronaphtho[1,2-c]pyrrole-1-carboxylate (13). Lead tetraacetate (7.36 g) was added in portions to a stirred solution of benzyl 4,5-dihydro-3-methylnaphtho[1,2-c]pyrrole-1-carboxylate (**9b**; 5.00 g) in glacial acetic acid (1.00 L) and acetic anhydride (50 ml) and the resulting mixture was stirred for 3 hr at room temperature. The solution was poured into ice/water (2 L), the aqueous solutions saturated with sodium chloride, and the resulting mixture allowed to stand for 30 min. The resulting precipitate was filtered off and washed thoroughly with water. The product was dissolved in chloroform, dried over sodium sulfate, filtered and the solvent evaporated under reduced pressure. The residual oil crystallized from dichloromethane-hexane to give the acetoxymethylpyrrole **13** (3.586 g; 61%) as an off-white solid, mp 116-118°C. Further crystallization gave an analytical sample, mp 119-120°C; IR (nujol mull): v 3385 (NH str.), 1727 (acetoxy C=O str.), 1664 (pyrrole C=O str.) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.07 (3H, s, $OCOCH_3$), 2.64 (2H, t, J = 6.8 Hz), 2.82 (2H, t, J = 6.8 Hz) (CH_2CH_2), 5.04 (2H, s, CH_2OAc), 5.35 (2H, s, OCH_2), 7.1-7.25 (3H, m, 6, 7 and 8-H), 7.3-7.45 (5H, m, Ph), 8.40 (1H, t, 9-H), 9.30 (1H, br, NH); ^{13}C NMR ($CDCl_3$): δ 19.80, 20.88, 30.67, 56.61, 66.26, 117.10, 123.89, 125.16, 126.47, 126.97, 127.58, 127.91, 128.31, 128.50, 128.59, 130.31, 135.94, 137.23, 160.41, 171.63.

Anal. calc. for $C_{23}H_{21}NO_4$: C, 73.57; H, 5.65; H, 3.73. Found: 73.14; H, 5.76; N, 3.81.

Benzyl 3-(5-Benzyloxycarbonyl-3-ethyl-4-methylpyrrolylmethyl)-3,4-dihydronaphtho[1,2-c]pyrrole-1-carboxylate (15). A solution of **13** (1.00 g) and benzyl 4-ethyl-3-methylpyrrole-2-carboxylate[18,21] (**14**; 0.66 g) in dichloromethane (60 mL) was vigorously stirred with K-10 Montmorillonite clay (4.00 g) at room temperature for 2 hr. The clay catalyst, which had turned a dark red color, was filtered off and washed well with dichloromethane. Evaporation of the solvent under reduced pressure gave a viscous oil which crystallized from ethanol to give the required dipyrrole **15** (892 mg; 60%) as a white powder, mp 159-161°C. Further crystallization from ethanol gave an analytical sample, mp 166-168°C. IR (nujol mull): v 3330 (NH str.), 1696 (C=O str.), 1643 (C=O str.) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.01 (3H, t, CH_2CH_3), 2.26 (3H, s, pyrrole-CH_3), 2.42 (2H, q, CH_2CH_3), 2.61 (2H, t), 2.86 (2H, t) (CH_2CH_2), 3.75 (2H, s, bridge-CH_2), 5.20 (2H, s), 5.22 (2H, s) (2 x OCH_2), 7.05-7.3 (13H, m, 2 x Ph and 6,7,8-H), 8.43 (1H, d, 9-H), 9.78 (1H, br), 9.98 (1H, br) (2 x NH). ^{13}C NMR ($CDCl_3$): δ 10.88, 15.57, 17.29, 20.08, 22.39, 30.96, 65.94, 66.23, 115.73, 117.42, 120.67, 124.32, 126.46, 126.84, 127.41, 127.71, 127.89, 128.06, 128.31, 128.43, 130.50, 130.81, 135.64, 136.13, 137.29, 160.72, 162.64.

Anal. calc. for $C_{36}H_{34}N_2O_4$: C, 77.38; H, 6.15; N, 5.01. Found: C, 76.69; H, 6.09; N, 4.92.

3-(3-Ethyl-5-carboxy-4-methyl-2-pyrrolylmethyl)-4,5-dihydronaphtho[1,2-c]pyrrole-1-carboxylic acid (16). The foregoing dibenzyl ester **15** (0.50 g) was dissolved in ethanol containing 10 drops of triethylamine, and shaken with 10% palladium-charcoal (0.05 g) at room temperature and 40 psi for 16 hr. The catalyst was filtered off and the solvent evaporated under reduced pressure. The residue was taken up in 5% aqueous ammonia solution and cooled to 0°C in an ice-salt bath. The mixture was neutralized with glacial acetic acid, maintaining the temperature below 5°C, and allowed to stand for a further 30 min. The resulting precipitate was filtered off, washed with water to remove all traces of acid, and dried *in vacuo* to give the dicarboxylic acid **16** (0.30 g; 88%) as a pale pink powder, mp 99-100°C, dec. ^{1}H NMR ($CDCl_3$): δ 1.03 (3H, t, CH_2CH_3), 2.27 (3H, s, pyrrole-CH_3), 2.46 (2H, q, CH_2CH_3), 2.64 (2H, m), 2.84 (2H, t) (CH_2CH_2), 3.88 (2H, s, bridge CH_2), 7.0-7.2 (3H, m, 6,7,8-H), 8.45 (1H, d, 9-H), 10.78 (1H, br), 10.91 (1H, br) (2 x NH).

2,12,18-Triethyl-1,3,13,17,19-pentamethyl-8^1,8^2,10,23-tetrahydronaphtho[1,2-g]bilin Dihydrobromide (20). Dicarboxylic acid **16** (400 mg) was dissolved in trifluoroacetic acid (2 mL) and stirred for 10 min at room temperature. A solution of 4-ethyl-3,5-dimethylpyrrole-2-carboxaldehyde (**19**; 320 mg) in methanol (8 mL) was added, immediately followed by 30% HBr-acetic acid (1.6 mL), and the resulting deep red mixture was stirred at room temperature for 30 min. Anhydrous ether (35 mL) was added dropwise, and the resulting mixture stirred for an additional 2 hr. The precipitate was filtered off and washed well with ether. Upon vacuum drying overnight, the title compound (520 mg; 68%) was obtained as a red-brown powder, mp 210°C, dec. UV/Vis (CH_2Cl_2): λ_{max} ($\log_{10}\varepsilon$) 461 (4.93), 532 (4.83) nm. ^1H NMR ($CDCl_3$): δ 0.73 (3H, t), 1.09 (3H, t), 1.11 (3H, t) (3 x $CH_2C\mathit{H}_3$), 2.23 (3H, s), 2.29 (3H, s), 2.31 (3H, s) (3,13,17-CH_3), 2.4-2.55 (8H, m), 2.79 (2H, q) (5 x CH_2), 2.71 (3H, s), 2.76 (3H, s) (1,19-CH_3), 5.21 (2H, s, bridge-CH_2), 7.09 (1H, s), 7.60 (1H, s) (2 x =CH), 7.30 (3H, m), 7.51 (1H, d) (4 x naphthalene-H), 13.23 (1H, br), 13.33 (2H, br), 13.47 (1H, br) (4 x NH).

Anal. calc. for $C_{38}H_{46}N_4Br_2$: C, 63.50; H, 6.46; N, 7.80. Found: C, 62.80; H, 6.19; N, 7.34.

7,13,17-Triethyl-3^1,3^2-dihydro-8,12,18-trimethylnaphtho[1,2-b]porphyrin (17).

a. A solution of p-toluenesulfonic acid monohydrate (450 mg) in methanol (7.6 mL) was added to a stirred mixture of **16** (300 mg) and 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane-5,5'-dicarboxaldehyde (**18**; 216 mg) in dichloromethane (76 mL) and methanol (7.6 mL). After a few minutes, a deep orange-red solution was formed. The mixture was stirred overnight in the dark at room temperature; at this point spectral examination showed absorptions at λ_{max} 414, 555, 603 nm. A saturated solution of zinc acetate in methanol (8 mL) was added and the resulting mixture stirred at room temperature for 24 hr. Spectral examination showed the development of an intense Soret band at λ_{max} 407 nm. The mixture was evaporated to dryness under reduced pressure and taken up in 5% sulfuric acid-methanol. The resulting mixture was partitioned between chloroform and water. The two layers were separated and the aqueous phase was reextracted with chloroform. The combined organic solutions were washed with water, 3% aqueous ammonia solution and water, and evaporated to dryness on a rotary evaporator. The residue was chromatographed on grade 3 alumina, eluting with dichloromethane. The colored fractions were evaporated and further purified by chromatography on a grade 3 alumina column, eluting with dichloromethane, and the major red band was collected and recrystallized from dichloromethane-methanol to give **17** as purple crystals (178 mg; 44%), mp 275-276°C. HR MS calcd. for $C_{37}H_{38}N_4$: 538.3099. Found: 538.3105. UV/Vis (CH_2Cl_2): λ_{max} ($\log_{10}\varepsilon$) 401 (5.19), 505 (4.11), 543 (4.12), 573 (3.85), 629 (3.65) nm. ^1H NMR ($CDCl_3$): δ -3.55 (2H, br, 2 x NH), 1.88 (3H, m, 3 x $CH_2C\mathit{H}_3$), 3.61 (3H, s), 3.63 (3H, s), 3.67 (3H, s) (3 x porphyrin-CH_3), 3.6-3.7 (2H, triplet obscurred by overlapping singlets, $C_6H_4C\mathit{H}_2$) 4.09 (6H, m, 3 x $C\mathit{H}_2CH_3$), 4.29 (2H, t, J = 7.3 Hz, porphyrin-$C\mathit{H}_2CH_2$), 7.50 (1H, t), 7.71 (1H, d, J = 7.3 Hz), 7.77 (1H, t), 9.00 (1H, d, J = 7.7 Hz) (C_6H_4), 10.06 (1H, s), 10.07 (1H, s), 10.12 (1H, s), 10.64 (1H, s) (4 x *meso*-H).

b. a,c-Biladiene **20** (400 mg) was added to a stirred solution of copper(II) chloride (1.125 g) in dimethylformamide (190 mL). The solution was stirred in the dark at room temperature for 2 hrs. The mixture was diluted with dichloromethane (250 mL) and washed with water (3 x 300 ml). Each of the aqueous layers was back extracted with dichloromethane, and the organic layers were combined, dried over sodium sulfate, filtered, and the solvent removed on a rotary evaporator, first under aspirator pressure and then using a vacuum pump. The residue was taken up in 10% v/v sulfuric acid/trifluoroacetic acid (50 ml) and stirred at room temperature for 45 min. The solution was diluted with dichloromethane, and washed with water, 5% aqueous sodium bicarbonate solution and water. The solvent was evaporated under reduced pressure, and the residue chromatographed on grade 3 alumina, eluting with dichloromethane. The main red fraction was evaporated and the residue recrystallized from dichloromethane-ethanol to give the dihydronaphthoporphyrin **17** (112 mg; 37%) as a purple powder, mp 274-276°C.

7,13,17-Triethyl-8,12,18-trimethylnaphtho[1,2-b]porphyrin (8). Dihydronaphthoporphyrin **17** (50 mg) was refluxed with DDQ (22 mg) in toluene (25 ml) for 15 min. The solvent was evaporated under reduced pressure and the residue chromatographed on a silica column eluting with dichloromethane. Crystallization of the major fraction from chloroform-methanol gave the title porphyrin as purple crystals (38 mg; 76%), mp 325-330°C, dec. EI MS: m/e (Relative abundance) 536 (M^+, 100%), 521 (M - CH_3, 13%); HR MS calcd. for $C_{37}H_{36}N_4$: 536.2943. Found: 536.2918. UV/Vis (CH_2Cl_2): λ_{max} ($\log_{10}\varepsilon$) 394 (infl., 5.04), 415 (5.31), 511 (3.99), 547 (4.46), 574 (4.03), 630 (3.76) nm. ^1H NMR ($CDCl_3$): δ -3.91 (2H, br, 2 x NH), 1.83-1.92 (9H, m, 3 x $CH_2C\mathit{H}_3$), 3.54 (3H, s), 3.65 (3H, s), 3.73 (3H, s) (3 x porphyrin-CH_3), 4.00 (2H, q), 4.14 (4H, q) (3 x β-CH_2), 7.81 (1H, t), 8.09 (1H, t), 8.37 (1H, d), 8.40 (1H, d), 9.35 (1H, d), 9.97-10.05 (1H, m) (6 x naphthalene-H), 9.99 (1H, s), 10.02 (1H, s), 10.34 (1H, s), 10.95 (1H, s) (4 x *meso*-H). ^1H NMR (TFA-$CDCl_3$): δ -3.56 (2H, br), -3.34 (1H, br), -3.0 (1H, v br), -

2.95 (1H, br) (4 x NH), 1.74 (3H, t), 1.78 (3H, t), 1.81 (3H, t) (3 x CH_2CH_3), 3.66 (3H, s), 3.68 (3H, s), 3.74 (3H, s) (3 x porphyrin-CH_3), 4.1-4.25 (6H, m, 3 x β-CH_2), 8.09 (1H, t), 8.36 (1H, t), 8.57 (1H, d), 8.89 (1H, d), 9.62 (1H, d), 10.00 (1H, d) (6 x naphthalene-H), 10.65 (1H, s), 10.66 (1H, s), 11.09 (1H, s), 11.51 (1H, s) (4 x *meso*-H).

Acknowledgements: This material is based upon work supported by the National Science Foundation under Grant No. CHE-9201149, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Fund of Illinois State University. C.P.D. received an Undergraduate Research Award in support of these studies from Baxter Healthcare Corp. for the spring semester of 1990. We also thank the National Science Foundation (Grant No. CHE-9001175) for providing funds to purchase a 300 MHz NMR spectrometer.

REFERENCES

1. Part 4: Quizon-Colquitt, D.M.; Lash, T.D. *J. Heterocyclic Chem.* **1993**, *30*, 477-482.
2. Results presented, in part, at the Baxter Healthcare Undergraduate Research Symposium (Denny, C.P.; Lash, T.D. Paper No. 13), Round Lake, Illinois, March 15, 1990; 204th National Meeting of the American Chemical Society, Washington D.C., August 1992 (Abstract: Lash, T.D.; Bellettini, J.R.; Shiner, C.M.; Denny, C.P. *Book of Abstracts*, GEOC 60); 85th Annual Meeting of the Illinois State Academy of Science, Sangamon State University, Springfield, Illinois, October 1992 (Abstract: Roper, T.J.; Denny, C.P.; Lash, T.D. *Trans. Ill. St. Acad. Sci.* **1992**, *Suppl. to Vol. 85*, p. 46, Abstract No. 45).
3. a. Howe, W.W. *Anal. Chem.* **1961**, **33**, 255-260. b. Thomas, D.W.; Blumer, M. *Geochim. Cosmochim. Acta* **1964**, *28*, 1147-1154. c. Millson, M.F.; Montgomery, D.S.; Brown, S.R. *Geochim. Cosmochim. Acta* **1966**, *30*, 207-222.
4. a. Baker, E.W. *J. Am. Chem. Soc.* **1966**, *88*, 2311-2315. b. Baker, E.W.; Yen, T.F.; Dickie, J.P.; Rhodes, R.E.; Clark, L.F. *J. Am. Chem. Soc.* **1967**, *89*, 3631-3639.
5. a. Clezy, P.S.; Fookes, C.J.R.; Mirza, A.H. *Aust. J. Chem.* **1977**, *30*, 1337-1347. b. Clezy, P.S.; Mirza, A.H. *Aust. J. Chem.* **1982**, *35*, 197-209. c. Clezy, P.S.; Leung, C.W.F. *Aust. J. Chem.* **1993**, *46*, 1705-1710.
6. a. Lash, T.D. *Energy Fuels* **1993**, *7*, 166-171. b. It has been suggested that bacteriochlorins are thermodynamically favored over isobacteriochlorins because they retain the symmetrical inside-outside 18π-electron delocalization pathway found in the porphyrins, and some evidence for the preferential formation of bacteriochlorins in cycloaddition reactions has been presented.[10d]
7. Kaur, S.; Chicarelli, M.I.; Maxwell, J.R. *J. Am. Chem. Soc.* **1986**, *108*, 1347-1348.
8. Verne-Mismer, J.; Ocampo, R.; Callot, H.J.; Albrecht P. *J. Chem. Soc., Chem. Commun.* **1987**, 1581-1583.
9. Baker, E.W.; Palmer, S.E. In *The Porphyrins* , Ed. Dolphin, D., Vol. 1, pp. 486-552, **1978**, Academic Press, New York.
10. a. Callot, H.J.; Johnson, A.W.; Sweeney, A. *J. Chem. Soc., Perkin Trans. I*, **1973**, 1424-1427. b. DiNello, R.K.; Dolphin, D. *J. Org. Chem.* **1980**, *45*, 5196-5204. c. Pangka, V.S.; Morgan, A.R.; Dolphin D. *J. Org. Chem.* **1986**, *51*, 1094-1100. d. Cavaleiro, J.A.S.; Jackson, A.H.; Neves, M.G.P.M.S.; Rao, K.R.N. *J. Chem. Soc., Chem. Commun.* **1985**, 776-777. e. Morgan, A.R.; Pangka, V.S.; Dolphin D. *J. Chem. Soc., Chem. Commun.* **1984**, 1047-1048. f. Yon-Hin, P.; Wijesekera, T.P.; Dolphin D. *Tetrahedron Lett.* **1989**, *30*, 6135-6138. g. Yon-Hin, P.; Wijesekera, T.P.; Dolphin, D. *Tetrahedron Lett.* **1991**, *32*, 2875-2878. h. Pandey, R.K.; Shiau, F.-Y.; Ramachandran, K.; Dougherty, T.J.; Smith, K.M. *J. Chem. Soc., Perkin Trans. I* **1992**, 1377-1385.
11. Bidigare, R.R.; Kennicutt, M.C., II, Ondrusek, M.E.; Keller, M.D.; Guillard, R.R.L. *Energy Fuels* **1990**, *4*, 653-657.
12. Yen, T.F. In *The Role of Trace Metals in Petroleum*; Yen, T.F., Ed.; Ann Arbor Science Publ., Ann Arbor, **1975**, pp 1-30.
13. Lash, T.D. In *Advances in Nitrogen Heterocycles*, Vol. 1; Moody, C.J., Ed.; JAI Press, in press.
14. a. Lash, T.D. *Organic Geochem.* **1989**, *14*, 213-225. b. Lash, T.D.; Balasubramaniam, R.P.; Catarello, J.J.; Johnson, M.C.; May D.A., Jr.; Bladel, K.A.; Feeley, J.M.; Hoehner, M.C.; Marron, T.G.; Nguyen, T.H.; Perun, T.J., Jr.; Quizon, D.M.; Shiner, C.M.; Watson, A. *Energy Fuels* **1990**, *4*, 668-674. c. Lash, T.D.; Quizon-Colquitt, D.M.; Shiner, C.M.; Nguyen, T.H.; Hu, Z. *Energy Fuels* **1993**, *7*, 172-178.
15. a. Lash, T.D.; Perun, T.J., Jr. *Tetrahedron Lett.* **1987**, *28*, 6265-6268. b. Lash, T.D. *Tetrahedron Lett.* **1988**, *29*, 6877-6880. c. Lash, T.D.; Johnson, M.C. *Tetrahedron Lett.* **1989**, *30*, 5697-5698. d. Lash, T.D.; Balasubramaniam, R.P. *Tetrahedron Lett.* **1990**, *31*, 7545-7548.
16. May, D.A., Jr.; Lash, T.D. *J. Org. Chem.* **1992**, *57*, 4820-4828.
17. a. Lash, T.D.; Bladel, K.A.; Johnson, M.C. *Tetrahedron Lett.* **1987**, *28*, 1135-1138. b. Lash, T.D.; Bladel, K.A.; Shiner, C.M.; Zajeski, D.L.; Balasubramaniam, R.P. *J. Org. Chem.* **1992**, *57*, 4809-4820.
18. Lash, T.D.; Catarello, J.J. *Tetrahedron* **1993**, *49*, 4159-4172.
19. Mataka, S.; Takahashi, K.; Tsuda, Y.; Tashiro, M. *Synthesis* **1982**, 157-159.
20. Paine, J.B., III; Dolphin, D. *J. Org. Chem.* **1985**, *50*, 5598-5604.
21. Lash, T.D.; Bellettini, J.R.; Bastian, J.A.; Couch, K.B. *Synthesis* **1994**, 170-172.
22. Jackson, A.H.; Pandey, R.K.; Rao, K.R.N.; Roberts, E. *Tetrahedron Lett.* **1985**, *26*, 793-796.
23. Arsenault, G.P.; Bullock, E.; MacDonald, S.F. *J. Am. Chem. Soc.* **1960**, *82*, 4384-8389.
24. Smith, K.M.; Minnetian, O.M. *J. Chem. Soc., Perkin Trans. I* **1986**, 277-280.
25. Lash, T.D.; Roper, T.J.; Novak, B.H.; Lin, Y. *Book of Abstracts for the 207th National Meeting of the American Chemical Society, San Diego, CA* **1994**, ORGN 154. Novak, B.H.; Lash, T.D. *Book of Abstracts for the 208th National Meeting of the American Chemical Society, Washington D.C.* **1994**, ORGN 222. Lash, T.D.; Novak, B.H.; Roper, T.J. *Ibid.*, GEOC 12. See also: Lash, T.D.; Novak, B.H.; Lin, Y. *Tetrahedron Lett.* **1994**, *35*, 2493; Lash, T.D.; Roper, T.J. *Tetrahedron Lett.*, in press.

(*Received in USA* 18 *July* 1994; *accepted* 24 *October* 1994)