TABLE II
GLC/MASS SPECTRAL ANALYSES FOR PRODUCTS FROM THE PHOTOCYCLIZATION

Substitution in aniline	10-Phenyl-10,9-borazarophenanthrenes (*m/e* values)
N-Acetyl	Unsubstituted[a] (255)
2-Bromo	Unsubstituted[a] (255) + 8-bromo (333)
2,5-Dimethyl	7-Methyl[a] (269) + 5,8-dimethyl (283)
2,6-Dimethyl	8-Methyl[b,c] (269)
3,5-Dimethyl	5,7-Dimethyl (283)

[a] These compounds had identical uv spectra and glc retention times with those listed in Table I. [b] Reference 2. [c] This derivative was isolated in 35% yield, mp 94–96°.

The procedure described here provides a simple, novel route to substituted borazarophenanthrenes. In addition it may well prove convenient for the facile ortho phenylation of amines to yield various 2-aminobiphenyl derivatives, since the heterocyclic compounds readily deboronate in cold sulfuric acid.[3] As mentioned earlier, the synthesis of substituted 2-aminobiphenyls is a very laborious procedure. This type of synthesis also offers an attractive route to other condensed borazarohydrocarbons through suitable choice of diaryl boron halide and aromatic amine. These areas are under investigation and will be reported later.

Experimental Section

General.—All melting points are corrected. Spectra were determined with Cary Model 15 (uv) and Varian A-60 (nmr) instruments. Mass spectra were determined with a CEC 21-110B instrument, equipped with a heated inlet system as described by Caldecourt[11] but constructed of glass.

Analytical glpc was performed using an F & M Model 720 gas chromatograph equipped with a 0.25 in. × 10 ft column packed with 10% UCW 98 on Chromosorb W.

Materials.—Eastman grade amines were used without further purification but were thoroughly dried in the photoreactor. Chlorodiphenylborane was prepared by the method of Niedenzu, Beyer, and Dawson.[12]

Photocyclizations.—The horizontal thin-film photochemical reactor described earlier was used in these experiments.[13] A second side arm was added to facilitate the addition of solid elemental iodine to the reactor. The amines (10 mmol) were placed in the flask, which was then pumped out with gentle warming (infrared lamp) for 1 hr. It was filled with dry nitrogen and reevacuated, and the process was repeated. Finally 600 ml of dry cyclohexane was distilled off sodium hydride into the reactor. Chlorodiphenylborane (5 mmol) was then injected into the flask and the mixture was rotated for 0.5 hr at room temperature. Iodine (11 mmol) was introduced while a generous flow of dry nitrogen was passing through the flask. The solutions were irradiated using a Hanovia 100-W 608A-36 lamp in a quartz insert. The progress of the reaction was followed by withdrawing 100-μl samples, diluting them in methanol (3 ml) containing a trace of sodium sulfite, and examining the uv spectra. After 15–20 hr the concentration of the desired species usually reached a maximum and the cyclohexane solution was washed with three 200-ml portions of water, three 100-ml portions of dilute HCl, two 50-ml portions of sodium sulfite solution, three 100-ml portions of dilute sodium hydroxide solution, and finally two 100-ml portions of water. The cyclohexane was then dried and evaporated. The crude product was either passed through a short pad of silica and recrystallized from ligroin (bp 63–75°) or recrystallized immediately from ligroin (bp 63–75°). Physical data are listed in Table I.

(11) V. J. Caldecourt, *Anal. Chem.*, **27**, 1670 (1955).
(12) K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).
(13) J. L. R. Williams and P. J. Grisdale, *Chem. Ind. (London)*, 1477 (1968).

Synthesis of the Zinc(II) Chelate of 6-(α-Hydroxy-β-carbomethoxyethyl)pyrroporphyrin Methyl Ester

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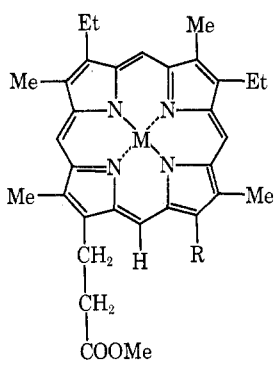
A porphyrin model compound with a β-ketopropionic acid side chain in the 6 position should be of interest since ring closure might take place between this side chain and the adjacent meso position forming a five-membered isocyclic ring. If such a ring closure takes place readily, a hypothesis concerning the biosynthesis of the isocyclic ring of the structurally similar chlorophyll may be advanced.

A β-hydroxypropionic acid derivative would be a convenient intermediate for this purpose and could be obtained from the corresponding formyl compound, using the Reformatsky reaction.

$$\text{porphyrin—CHO} + \text{BrCH}_2\text{COOCH}_3 + \text{Zn} \longrightarrow [\text{porphyrin—CH(OZnBr)CH}_2\text{COOCH}_3] \longrightarrow \text{porphyrin—CH(OH)CH}_2\text{COOCH}_3$$

Accordingly, 6-formylpyrroporphyrin methyl ester (**5**) was prepared from pheophytin (**1**). The conditions used were essentially those of Fischer[1] and Vida.[2] Compound **1** was degraded to pyrroporphyrin methyl ester (**2**). Compound **2** was converted to its Zn(II)



2, R = H; M = 2H
3, R = H; M = Zn
4, R = H; M = Fe
5, R = CHO; M = 2H
6, R = CHO; M = Zn
7, R = CH[OH]CH_2COOMe; M = Zn
8, R = CH=CHCOOMe; M = Zn

chelate **3** with zinc diacetate in acetic anhydride. Attempts to formylate the Zn(II) chelate were unsuccessful; therefore compound **3** was converted into the Fe(II) chelate **4** with ferrous acetate.

Compound **4** was formylated with dichloroethoxyethane in the presence of stannic chloride to yield the 6-formyl compound which in turn was converted to the Zn(II) chelate of 6-formylpyrroporphyrin methyl ester (**6**) with zinc diacetate.

In the Reformatsky reaction, compound **6** was treated with bromoacetic methyl ester to yield the Zn(II) chelate of 6-(α-hydroxy-β-carbomethoxyethyl)pyrropor-

(1) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Leipzig, 1937.
(2) J. Vida, Research Report, Harvard University, Cambridge, Mass., 1962.

phyrin methyl ester (7) as the major product. In the course of this reaction relatively mild conditions were used to avoid further reaction or hydrolysis of the relatively unstable allylic alcohol produced in the reaction.

Experimental Section

Pyrroporphyrin Methyl Ester (2).—Pheophytin (5-g portions) was heated in an autoclave for 16 hr with 40.0 g of potassium hydroxide in 50 ml of methanol. The temperature was carefully maintained at 145–150°. The reaction mixture was cooled and transferred to a 500-ml flask using methanol and water. The solution was evaporated; the residue was dissolved in 40 ml of methanol and 60 ml of water and acidified, with cooling to pH 6 with 10% aqueous hydrochloric acid (*ca.* 240 ml was needed). A precipitate separated. It was filtered, dried at room temperature, dissolved in 30 ml of pyridine, and further diluted with 800 ml of ether. The organic layer was extracted thoroughly first with *ca.* 1 l. of 1% and then with *ca.* 2 l. of 2% aqueous hydrochloric acid. Since some material precipitated during the acid extraction, it was important to filter the acid extracts. They were neutralized with concentrated ammonium hydroxide to pH 4 and extracted thoroughly with chloroform. The chloroform extracts were washed with water and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to yield a solid. The solid residue (1.2–1.5 g) was dissolved in 100 ml of chloroform and treated with a 5 *M* excess of ethereal diazomethane at 0° for 1 hr. The solvents were then removed under reduced pressure, and the residue was dissolved in 20 ml of warm dichloromethane and 40 ml of methanol. The solution was cooled overnight. On filtration, 1 g of **2** was obtained. The mother liquors gave an additional 150–200 mg. From 18 g of pheophytin, 4 g (22%) of crystalline **2** was obtained: λ_{max} (chloroform) 498, 531, 566, 618 mμ. This material showed several spots on tlc and was purified as its Zn(II) chelate.

Zn(II) Chelate of Pyrroporphyrin Methyl Ester (3).—The crude pyrroporphyrin methyl ester (350 mg) and $Zn(OAc)_2 \cdot 2H_2O$ (350 mg) were dissolved in a mixture of 100 ml of acetic acid and 10 drops of acetic anhydride. The solution was refluxed for 30 min under nitrogen. The solvents were distilled off under reduced pressure, and the residue was dissolved in 50 ml of chloroform. The chloroform solution was washed with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated. This solution was chromatographed on a 10-g silica gel column (prepared in chloroform) and eluted with chloroform. The middle fractions gave the purest material: mp 235–237° (dichloromethane–methanol); λ_{max} (chloroform) 532 and 568 mμ; ir (KBr pellet) 5.74 μ (ester C=O).

Fe(II) Chelate of Pyrroporphyrin Methyl Ester (4).—The Zn(II) chelate of pyrroporphyrin methyl ester (1.2 g) was dissolved in 70 ml of acetic acid. To this solution was added a hot solution of ferrous acetate prepared by refluxing 1.2 g of ferrous chloride ($FeCl_2 \cdot 4H_2O$), 1.0 g of sodium acetate, and 100 mg of *ferrum reductum* in 140 ml of acetic acid under nitrogen for 20 min followed by filtration. The reaction solution was refluxed 10 min under nitrogen and then 20 min exposed to dry air. The cooled solution was poured into water; the resulting precipitate was filtered off, washed with a large volume of water, and dried. The crude yield was 1.33 g (100%).

Dichloroethoxymethane.—Phosphorus pentachloride (120.0 g) was placed in a round-bottom flask equipped with a reflux condenser and a funnel. Freshly distilled ethyl formate (80 ml) was added dropwise to the phosphorus pentachloride, allowed to stand until solution was complete, and then refluxed for 1 hr. The mixture was distilled and the fraction boiling at 105–108° (760 mm) was collected (105 g) and used.

6-Formylpyrroporphyrin Methyl Ester (5).—Compound **4** (500 mg) was dissolved in 70 g of dichloroethoxymethane, bp 105–108°. The solution was warmed to 55° in a water bath, and 250 mg of stannic chloride was added dropwise and stirred at 55° for 10 min. An additional 250 mg of stannic chloride was added dropwise and stirring was continued for an additional 10 min. The reaction mixture was poured on 600–800 g of ice while stirring vigorously. After 30–60 min a flocculent precipitate separated which was filtered and dried. The crude yield was *ca.* 550 mg. The dry residue was dissolved in 25 ml of concentrated sulfuric acid at room temperature, stirred for 10 min, and poured onto 200 g of ice. *Ca.* 40 ml of concentrated ammonium hydroxide was added with cooling, and the mixture was extracted with chloroform. The extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated to *ca.* 10 ml. Ether (600 ml) was added. The ether–chloroform solution was washed with 1 l. of 1.5% aqueous hydrochloric acid and the aqueous layer was discarded. The ether–chloroform solution containing compound **5** was repeatedly extracted with 7% aqueous hydrochloric acid.

To the hydrochloric acid extracts containing compound **5** concentrated ammonium hydroxide was added to adjust the pH to 4. Compound **5** was extracted to chloroform and the chloroform solution was washed with water and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in 15 ml of chloroform and 25 ml of methanol and cooled overnight to give 200 mg (40%) of **5**: mp 240°; ir (KBr pellet) 5.74 (ester C=O), 6.02 μ (aldehyde C=O); λ_{max} (chloroform) 515, 556, 578, 636 mμ. The tlc of compound **5** showed traces of two to three other substances.

Zn(II) Chelate of 6-Formylpyrroporphyrin Methyl Ester (6).—Compound **5** (300 mg) was dissolved in 50 ml of acetic acid. $Zn(OAc)_2 \cdot 2H_2O$ (300 mg) was added, followed by 10 drops of acetic anhydride. The mixture was stirred with reflux under nitrogen for 30 min and concentrated. The solution was diluted with chloroform and then washed thoroughly with saturated sodium bicarbonate and water. The chloroform solution was dried and the solvent was evaporated under reduced pressure. The residue was dissolved in 2 ml of methanol and 2 ml of dichloromethane and cooled. The yield was 240 mg (70%): mp 221–223°; λ_{max} (chloroform) 554 and 600 mμ. Chromatography of the mother liquors using Florisil gave an additional small amount of crystalline material.

Zn(II) Chelate of 6-(α-Hydroxy-β-carbomethoxyethyl)pyrroporphyrin Methyl Ester (7). The Reformatsky Reaction.[3]—Activated zinc[4] (300 mg) was placed in a three-neck flask, equipped with a magnetic stirrer and a reflux condenser. The zinc was heated for 1 hr at 110° under a stream of nitrogen. The flask was then cooled to room temperature; 15 ml of absolute tetrahydrofuran was added, followed by 0.8 ml of freshly distilled bromomethyl acetate. After the dissolution of zinc was completed (*ca.* 10–15 min), 130 mg of **6**, predried at 80° (0.1 mm) for 1 hr, was added in one portion. After 10 min the reaction was essentially complete. Chloroform (50 ml) was added to the reaction mixture and the reaction was cooled to 0°. At this temperature 5 ml of 10% sulfuric acid was added, and the reaction mixture was stirred vigorously for 30 min.

Then the chloroform layer containing compound **7** was washed with a 6% sodium bicarbonate solution and then water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was dissolved in a small volume of chloroform and chromatographed on a preparative silica gel tlc plate (0.75-mm thickness) using chloroform. After 5–8 hr, three main zones were separated, which were scraped off separately and extracted with chloroform–methanol (1:1). Three major products were thus obtained.

Compound **8**: red-brown rhombic plates; mp 232–233° (dichloromethane–chloroform); on tlc largest R_f, a green zone; ir (KBr pellet) 6.2 μ; λ_{max} (chloroform) 548 and 593 mμ; Zn-free material, λ_{max} (chloroform) 508, 550, 570, 638 mμ; yield 27.0 mg.

Compound **7**: micro red needles; mp 225–227° (chloroform–ether); on tlc very small R_f, a red zone; ir (KBr pellet) 2.8 (OH stretching), 5.74 (ester C=O), 7.0 μ; λ_{max} (THF) 500 mμ (ε 1930), 535 (11,750), 573 (12,710); yield 39.0 mg (26.7%).

Anal. Calcd for $C_{36}H_{40}O_5N_4Zn$: C, 64.14; H, 5.98; N, 8.31. Found: C, 63.71; H, 5.97; N, 7.89.

Unidentified compound: red-brown plates; mp 250–253° (chloroform–methanol); on tlc intermediate R_f, a green zone; ir (KBr pellet) 6.05 μ; λ_{max} (chloroform) 548 and 593 mμ; yield 25.0 mg.

Registry No.—**2**, 5174-83-4; **3**, 31635-80-0; **4**, 31635-81-1; **5**, 31635-82-2; **6**, 31705-56-3; **7**, 31635-83-3; **8**, 31635-84-4.

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