action course; a mixture of XV and XVI was still obtained in about 95% (crude) or 83% (distilled) yield.

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Octaarylporphyrins[1]

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A synthesis is described of 3,4-diarylpyrroles-2,5-dicarboxylic acids from benzils and dimethyl-N-acetyliminodiacetate catalyzed by sodium methoxide. Decarboxylation of the pyrrole diacids yields 3,4-diarylpyrroles. Aliphatic diketones except dimethyl oxalate do not undergo the pyrrole condensation. Octaarylporphyrins were synthesized in excellent yields from the Mannich bases of 3,4-diphenylpyrrole and 3,4-di-*p*-methoxyphenylpyrrole. Physical and spectral characteristics of these porphyrins and some of their metallo derivatives are described.

In connection with a study of substitution reactions of oxidized and reduced porphyrins,[3] it appeared desirable to prepare a symmetrically substituted model porphyrin because the number of theoretically possible positional isomers that could result would be kept at a minimum. A literature survey[4] indicated that only a few octaalkyl- and no octaarylporphyrins were known. The most outstanding characteristic of the symmetrically substituted octaalkylporphyrins is their low solubility in the usual organic solvents. This property is probably due to the tight crystalline packing of these molecules. Inspection of models of 1,2,3,4,5,6,7,8-octaphenylporphine[5] (V) revealed that the phenyl groups should take up conformations in which their planes are oriented 35 to 45° out of the plane of the porphyrin ring. This feature of the molecule was quite desirable for two reasons. The bulky out-of-plane phenyl groups would protect the methine bridges of the porphyrin ring from attack by oxidizing agents, thus permitting the oxidative removal of electrons from the π-orbitals of the macrocyclic ring system. In addition, the phenyl groups might cause a reduction in the tight crystalline packing of the molecules which would result in an increased solubility of the octaarylporphyrins as compared to the octaalkyl analogs.

Octaphenylporphine was synthesized from the previously unknown 3,4-diphenylpyrrole *via* the Linstead procedure.[4c] This pyrrole was prepared as outlined in Figure 1. When N-acetyliminodiacetate dimethyl ester was condensed with benzil in 10% sodium methoxide, a compound was isolated that had the expected properties of 3,4-diphenylpyrrole-2,5-dicarboxylic acid (I).[6] The pyrrole diacid shows the expected large carbonyl band in the infrared centered at 1680 cm.$^{-1}$. In addition to the OH stretching frequency due to the two carboxyl groups ranging from 2500–3000 cm.$^{-1}$, the compound has three absorption peaks in the NH stretching region at 3450, 3510, and 3600 cm.$^{-1}$. These may be due to the various hydrogen-bonded forms of the molecule.[7] Additional evidence for the suggested structure comes from the ultraviolet spectrum[8] ($\lambda_{\max}$ 245 and 284 mμ) and from the smooth, nearly quantitative decarboxylation of the diacid in ethanolamine to 3,4-diphenylpyrrole (II). The structure of II was confirmed by elementary analytical results, by the presence of an NH stretching frequency at 3390 cm.$^{-1}$ in the infrared, by the ultraviolet spectrum ($\lambda_{\max}$ 238 and 271 mμ), and from conversion of the pyrrole into magnesium octaphenylporphine (IV) as described below.

The scope of this pyrrole synthesis was extended by including the condensation of *p*-anisil, *p*-tolil, and *o*-tolil (see Figure 1). The yields with the first two compounds were high, but the low yield with *o*-tolil suggests steric hindrance of the *ortho*-methyl groups in the condensation. A variety of reaction conditions were unsuccessfully tried in an attempt to improve the yield with this diketone. The condensation could be made to take place with sodium hydride in benzene, but the yields were equally low. Only polymeric products resulted when the condensation with *o*-tolil was carried out with sodium hydride in xylene, sodium ethoxide in ethanol, or magnesium ethoxide in benzene.

Attempts to extend the pyrrole condensation with aliphatic diketones, such as biacetyl, failed because of the facile self-condensation of these compounds under basic conditions. However, dimethyl oxalate was an exception giving a 65% yield of 3,4-dihydroxy-2,5-dicarbomethoxypyrrole (Id). Recent spectroscopic evidence indicates that 3-hydroxypyrroles exist mainly in the keto form.[9] Compound Id was etherified with diazomethane to the corresponding 3,4-dimethoxy

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(1) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961; Abstracts p. 97Q.

(2) To whom inquiries should be made at Northern Regional Research Laboratory, Peoria, Ill.

(3) Mendel Friedman, Ph.D. Thesis, University of Chicago, March 1962.

(4) (a) H. Fischer and B. Wallach, *Ann.*, **450**, 164 (1926); (b) W. Siedel and F. Winkler, *ibid.*, **554**, 162 (1943); (c) U. Eisner, R. P. Linstead, E. A. Parkes, and E. Stephen, *J. Chem. Soc.*, 1655 (1956); (d) U. Eisner, A. Lichtarowich, and R. P. Linstead, *ibid.*, 733 (1957).

(5) The general term octaarylporphyrins will be used to name this porphyrin and analogous ones, but for specific porphyrins the term porphine will be used to describe the porphyrin ring system and octa, the eight substituents in the β-pyrrole positions.

(6) After the work on this pyrrole synthesis had been completed, K. Dimroth and U. Pintschovius [*Ann.*, **639**, 102 (1961)] published a similar pyrrole synthesis in which they use potassium *t*-butoxide as the catalyst. Their procedure results in a mixture of pyrroles due to transesterifications. These have to be separated chromatographically. None of the pyrroles described in this paper were prepared by these authors.

(7) (a) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 251; (b) J. Fog and E. Jellium, *Nature*, **198**, 88 (1963).

(8) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 14.

(9) R. S. Atkinson and E. Bullock, *Can. J. Chem.*. **41**, 625 (1963).

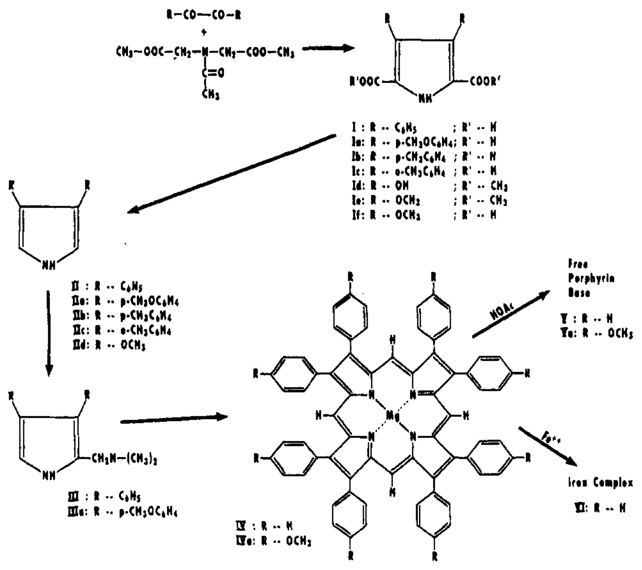

Figure 1.

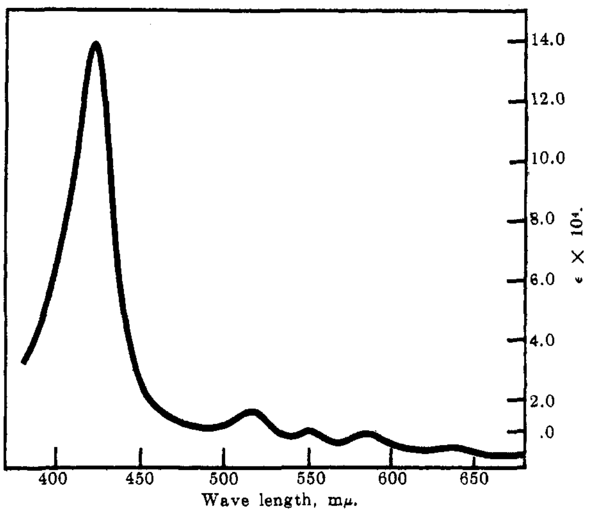

Figure 2.—Absorption spectrum of octaphenylporphine (V) in chloroform.

derivative Ie which was hydrolyzed in 2 *N* NaOH to the crude diacid If. Efforts to decarboxylate If to 3,4-dimethoxypyrrole (IId) yielded a compound which was quite unstable.

The 3,4-diphenylpyrrole was converted to the Mannich base III by means of formaldehyde and dimethylamine hydrochloride. On refluxing with 1 mole of ethylmagnesium bromide, compound III gave a nearly 50% yield of the desired magnesium octaphenylporphine (IV). The magnesium complex was converted with acetic acid into the free porphyrin base V. The structure of V was confirmed by a visible spectrum typical for a porphyrin[10] (Table I), its mode of formation, and elementary analytical results. The magnesium complex of octa(*p*-methoxyphenyl)porphine (IVa) and the free porphyrin base Va were prepared in the same manner as described for octaphenylporphine starting from 3,4-di(*p*-methoxyphenyl)pyrrole (IIa) *via* the Mannich base IIIa.

The visible spectra of octaarylporphyrins V and Va in neutral and acidic solvents and of metallo derivatives IV and VI in pyridine are illustrated in Figures 2–7.

TABLE I

VISIBLE SPECTRAL CHARACTERISTICS OF OCTAARYLPORPHYRINS AND DERIVATIVES

Compd.	Absorption, mμ	ε, l. mole⁻¹ cm.⁻¹
Magnesium octaphenylporphine (IV) in dimethylformamide	590	13,000
	550	19,000
Magnesium octa(*p*-methoxyphenyl)-porphine (IVa) in pyridine	600	15,000
	562	25,000
	438	285,000
Octaphenylporphine (V) in chloroform	635	3,000
	583	9,000
	550	11,000
	514	17,000
	423	138,000
Octa(*p*-methoxyphenyl)porphine (Va) in chloroform	638	6,000
	583	12,000
	555	17,000
	518	23,000
	424	330,000
Octaphenylporphine (V) in chloroform acidified with hydrochloric acid	615	5,000
	590 (shoulder)	5,500
	573	12,000
	442	142,000
Octa(*p*-methoxyphenyl)porphine (Va) in chloroform acidified with hydrochloric acid	625	15,000
	603 (shoulder)	17,000
	582	42,000
	535 (shoulder)	14,000
	446	283,000
Ferrioctaphenylporphine acetate (VI) in pyridine	562	16,000
	530	11,000
	432	139,000

In contrast to the observations of Eisner, *et al.*,[4c] with octaalkylporphyrins, no octaarylchlorins could be isolated from the described porphyrin syntheses, and it appears that, if chlorins are formed at all, they are readily oxidized to the corresponding porphyrins under the reaction conditions. This observation is not surprising since the extra hydrogens in the β-pyrrole positions of the porphyrin ring would be benzilic and easily oxidized.

The new porphyrins turned out to be only sparingly soluble in most organic solvents. They dissolved slightly in formic and acetic acids and to a greater extent in sulfuric acid, forming green solutions. The magnesium complexes IV and IVa and the iron complex VI were soluble in hot dimethylformamide and pyridine.

Because the porphyrin ring in the octaarylporphyrins is symmetrically substituted, there is no perturbation on the symmetry of the distribution of π-electrons to any one side of the ring, and both V and Va have the expected etio-type visible spectra.[10] The absorption maxima in the visible spectra of the two porphyrins differ slightly, although it is possible to write additional structures of the quinoid type contributing to the resonance hybrid of Va compared with V.[11] Based on the more effective stabilization of quinoid excited states by resonance,[12] the absorption maxima of Va should occur at longer wave lengths than corresponding values of V.

The spectral data imply that the aryl substituents are not completely coplanar with the porphyrin

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[10] S. Aronoff, *Chem. Rev.*, **47**, 178 (1950).

[11] J. G. Erdman and A. H. Corwin, *J. Am. Chem. Soc.*, **68**, 1885 (1946).

[12] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Chapter 6.

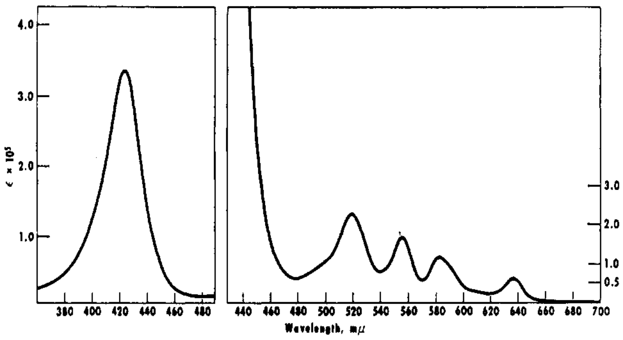

Figure 3.—Absorption spectrum of octa(*p*-methoxyphenyl)porphine (Va) in chloroform.

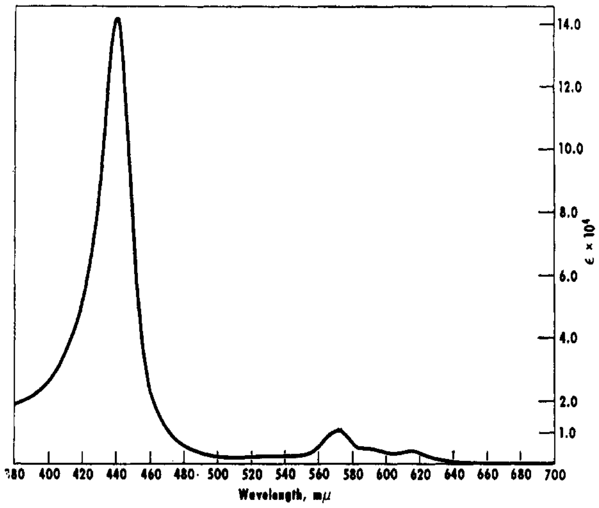

Figure 4.—Absorption spectrum of octaphenylporphine (V) in chloroform acidified with hydrochloric acid.

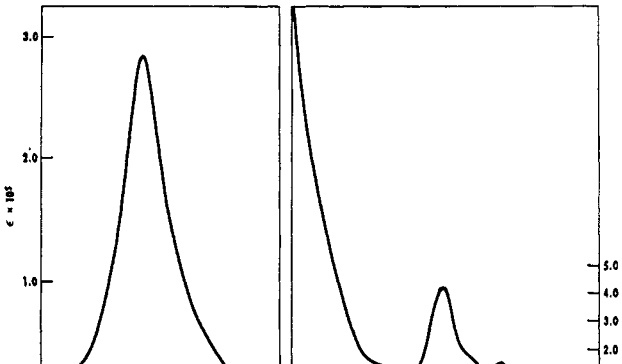

Figure 5.—Absorption spectrum of octa(*p*-methoxyphenyl)porphine (Va) in chloroform acidified with hydrochloric acid.

ring, as predicted from model studies; consequently, the noncoplanarity causes a steric inhibition of resonance between π-electrons of the aryl substituents and those of the porphyrin ring. It should be possible to determine the exact geometry of the octaarylporphyrin molecules by means of X-ray diffraction studies. Such studies were recently carried out for the somewhat analogous case of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine and its copper complex.[13]

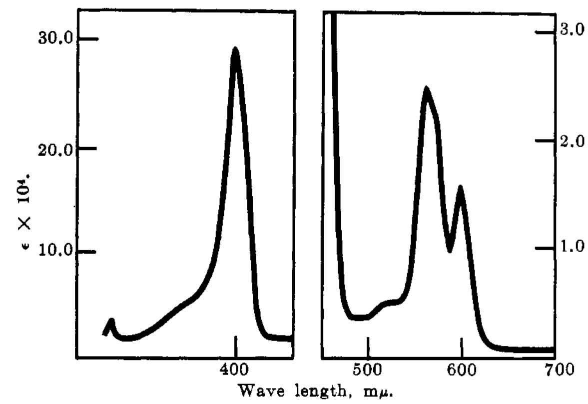

Figure 6.—Absorption spectrum of magnesium octa(*p*-methoxyphenyl)porphine (IVa) in pyridine.

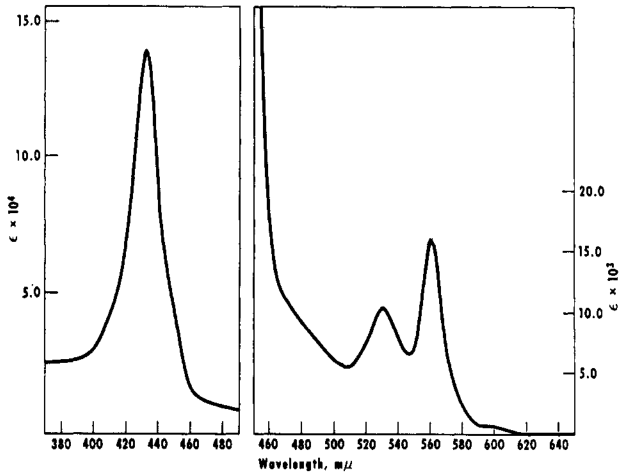

Figure 7.—Absorption spectrum of ferrioctaphenylporphine acetate (VI) in pyridine.

Experimental

Melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer from KBr pellets. Ultraviolet spectra of pyrroles were determined in ethanol and visible spectra of porphyrins in the solvents indicated in Table I on a Cary Model 14 spectrophotometer. The elementary analyses were performed by Mr. William Saschek.

Dimethyl N-Acetyliminodiacetate.—This compound was prepared from disodium iminodiacetic acid monohydrate (Eastman) in a 60% yield by a procedure similar to that described by Jongkees.[14] The compound melted sharply at 84°, lit.[14] m.p. 83–84°.

3,4-Diphenylpyrrole-2,5-dicarboxylic Acid (I).—Sodium (3 g.) was dissolved in 35 ml. of absolute methanol under an atmosphere of nitrogen in a 100-ml. three-necked flask equipped with a nitrogen inlet and reflux condenser. The solution was cooled to room temperature and 3 g. (0.014 mole) of dimethyl N-acetyliminodiacetate dissolved in 15 ml. of dry methanol was added to the sodium methoxide solution while the mixture was being stirred by means of a magnetic stirrer. This was followed by the addition of 6 g. (0.028 mole) of solid benzil. Stirring was continued at room temperature until all of the benzil was in solution. The reaction mixture was then slowly heated to the boiling point, refluxed for 25 min., and poured into 200 ml. of water. A yellow precipitate settled out at this point, and was filtered off. A melting point indicated that it was unchanged benzil. The cooled aqueous solution was extracted three times with ether to remove any dissolved benzil. The dissolved ether and methanol were removed by means of an aspirator, the aqueous solution was cooled in an ice bath, and neutralized with cold 2 *N* HCl. The precipitated pyrrole was filtered off immediately. The benzilic acid formed as a by-product stayed in solution at

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[13] (a) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964); (b) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *ibid.*, **85**, 2334 (1963); (c) E. B. Fleischer, *ibid.*, **85**, 1353 (1963).

[14] M. Jongkees, *Rec. trav. chim.*, **27**, 287 (1908).

this point. The hydrolysis of the pyrrole ester to the diacid was completed by refluxing it in 10% NaOH solution for 30 min. The basic solution was neutralized with 3 *N* HCl with cooling and the precipitated pyrrole diacid was recrystallized from acetic acid as white needles. The compound melted at 267–270° with decomposition: 2.22 g. (0.007 mole), 50% yield; λ_{max} 245 and 284 mμ (ϵ 16,300 and 11,600, respectively).

Anal. Calcd. for $C_{18}H_{13}NO_4$: N 4.56. Found: N, 4.46.

Decarboxylation of 3,4-Diphenylpyrrole-2,5-dicarboxylic Acid to 3,4-Diphenylpyrrole (II).—In a typical experiment 1 g. (3.26 mmoles) of the pyrrole diacid was placed into a 10-ml. pear-shaped flask equipped with a reflux condenser and nitrogen inlet. To this was added 2 ml. of ethanolamine and the flask was heated to 180° (bath temperature). The solution was refluxed for 45 min. to 1 hr. and the amount of carbon dioxide evolution was periodically tested with barium hydroxide solution. When carbon dioxide evolution was negligible, refluxing was discontinued, and the hot solution was poured into 50 ml. of water. The precipitated 3,4-diphenylpyrrole was filtered off, air-dried, and sublimed under vacuum at 90°. The compound melted sharply at 99°: 0.68 g. (2.94 mmoles), 90% yield; λ_{max} 238 and 271 mμ (ϵ 15,000 and 11,000, respectively).

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.67; H, 5.94; N, 6.39. Found: C, 87.63; H, 6.00; N, 6.21.

3,4-Di-*p*-methoxyphenylpyrrole-2,5-dicarboxylic Acid (Ia).—To a solution of 4.5 g. of sodium in 45 ml. of absolute methanol was added a solution of 3.1 g. (0.021 mole) of dimethyl N acetyliminodiacetate in 15 ml. of dry methanol and 3.6 g. (0.0133 mole) of 4,4′-dimethoxybenzil under an atmosphere of nitrogen and with stirring. As the solution was slowly heated, near the boiling point its color turned a deep purple. The reaction mixture was refluxed for 15 min. and poured into 150 ml. of water. The material was worked up as described for the 3,4-diphenylpyrrole-2,5-dicarboxylic acid. The pyrrole diacid was recrystallized from acetic acid as pinkish needles which melted at 218–220° with decomposition: 2 g. (0.005 mole), 70% yield; λ_{max} 253 and 283 mμ (ϵ 13,700 and 9000, respectively).

Anal. Calcd. for $C_{20}H_{17}NO_6$: N, 3.82. Found: N, 3.75.

3,4-Di-*p*-methoxyphenylpyrrole (IIa).—Five grams (0.0148 mole) of the diacid was refluxed in 12 ml. of ethanolamine for 90 min. The hot ethanolamine solution was poured into 150 ml. of water and the filtered pyrrole was air-dried and sublimed under vacuum at 115° (0.05 mm.) giving 3.4 g. (0.0124 mole), 82%, of pure 3,4-di-*p*-methoxyphenylpyrrole which melted sharply at 116° and had λ_{max} 260 and 235 mμ (ϵ 11,800 and 9000, respectively).

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.42; H, 6.09; N, 5.02. Found: C, 77.42; H, 6.20; N, 5.17.

3,4-Di-*p*-methylphenylpyrrole-2,5-dicarboxylic Acid (Ib).—The required 4,4′-dimethylbenzil was obtained in an over-all yield of 65% by subjecting *p*-tolualdehyde (Matheson) to the benzoin condensation and oxidizing the crude *p*-toluoin with copper sulfate in pyridine to the *p*-tolil.[15] The condensation was carried out with 2.5 g. (0.0106 mole) of 4,4′-dimethylbenzil and 3.1 g. (0.0212 mole) of dimethyl N-acetyliminodiacetate in 50 ml. of 10% sodium methoxide solution as described for the 3,4-diphenylpyrrole-2,5-dicarboxylic acid. The pyrrole diacid was recrystallized from acetic acid as colorless needles: m.p. 239–242° dec.; yield, 1.80 g. (0.0053 mole), 50% based on *p*-tolil; λ_{max} 247 and 283 mμ (ϵ 17,500 and 10,900, respectively).

Anal. Calcd. for $C_{20}H_{17}NO_4$: N, 4.18. Found: N, 4.13.

3,4-Di-*p*-methylphenylpyrrole (IIb).—A solution of 1.8 g. (5.35 mmoles) of 3,4-di-*p*-methylphenylpyrrole-2,5-dicarboxylic acid in 2 ml. of ethanolamine was refluxed for 1 hr. and the hot solution was poured into 50 ml. of water. The flask was placed in a cooler for 24 hr. and the precipitated pyrrole was filtered off, air-dried, and sublimed at 112° (0.05 mm.): m.p. 126°; yield, 1 g. (4.37 mmoles), 82%; λ_{max} 243 and 264 mμ (ϵ 13,600 and 12,700, respectively).

Anal. Calcd. for $C_{18}H_{17}N$: C, 87.45; H, 6.88; N, 5.67. Found: C, 87.07; H, 7.23; N, 5.47.

2,2′-Dimethylbenzil.—The 2,2′-dimethylbenzoin was previously prepared by Ahlquist and Ekencranz[16] but no yield is reported. In the following procedure the benzoin was not isolated but was directly oxidized to the benzil by copper sulfate and pyridine. To a solution of 25 ml. (0.20 mole) of *o*-tolualdehyde (Matheson) dissolved in 55 ml. of absolute ethanol was added 30 ml. of water and 5 g. of KCN. The reaction mixture was refluxed for 2 hr. and cooled somewhat; an additional 2 g. of KCN was added; refluxing was continued for another hour. The mixture was then poured into 200 ml. of water and kept in a cooler for 12 hr. The oily layer which settled out was separated from the cloudy aqueous layer. The aqueous layer was extracted once with 150 ml. of ether. The ether was removed and the residue was combined with the oily benzoin layer. The benzoin was not further purified but was directly oxidized to 2,2′-dimethylbenzil by refluxing for 2 hr. in a solution of 100 g. (0.40 mole) of copper sulfate pentahydrate in 160 ml. of pyridine and 50 ml. of water. The hot pyridine solution was then poured into 600 ml. of water and the benzil was extracted with five 200-ml. portions of boiling ether. The combined ether layers were washed twice with water. The ether was dried with magnesium sulfate and removed under vacuum. The residue was recrystallized from 60% ethanol yielding yellow needles which melted at 96°: over-all yield, 16.5 g. (0.067 mole), 35%; λ_{max} 260 mμ (ϵ 19,300).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.67; H, 5.72.

3,4-Di(*o*-methylphenyl)pyrrole (IIc).—2,2′-Dimethylbenzil 1.5 g. (6.3 mmoles) and 1.3 g. (6.3 mmoles) of dimethyl N-acetyliminodiacetate were condensed in 25 ml. of 10% sodium methoxide solution as described for 3,4-diphenylpyrrole-2,5-dicarboxylic acid. The crude diacid Ic (m.p. 240–245° dec.) was decarboxylated in the same manner as described for 3,4-diphenylpyrrole. After sublimation, 0.05 g. (0.21 mmole), an over-all yield of 2.5%, of 3,4-di-*o*-methylphenylpyrrole was obtained: m.p. 185–186°; λ_{max} 235 and 257 mμ (ϵ 15,600 and 9200, respectively).

Anal. Calcd. for $C_{18}H_{17}N$: C, 87.45; H, 6.88; N, 5.67. Found: C, 87.00; H, 7.06; N, 6.00.

The 2,2′-dimethylbenzilic acid methyl ester isolated from this pyrrole condensation was recrystallized from methanol and melted at 65°. The infrared spectrum of this compound shows a carbonyl absorption at around 1735 cm.$^{-1}$ and an OH absorption at 3400 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.55; H, 6.67. Found: C, 75.47; H, 6.73.

The 2,2′-dimethylbenzilic acid was obtained by refluxing the ester in 10% NaOH solution for 30 min. and precipitating the acid with 3 *N* HCl. The compound was air dried and recrystalized from methanol: m.p. 150°; CO- absorption at 1710 cm.$^{-1}$ and OH band at 3400 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.25. Found: C, 74.70; H, 6.43.

3,4-Dihydroxy-2,5-dicarbomethoxypyrrole (Id).—Into 30 ml. of a 10% $NaOCH_3$ solution in methanol was added a mixture of 3 g. (0.025 mole) of dimethyl oxalate and 3 g. (0.02 mole) of dimethyl N-acetyliminodiacetate in 20 ml. of dry methanol under an atmosphere of nitrogen and with stirring. The reaction mixture was refluxed for 30 min. and cooled to room temperature, and 10 ml. of acetic acid was added to it. The entire contents were then poured into 300 ml. of water and the resulting precipitate, 2.4 g., was filtered off. An additional 0.2 g. of pyrrole was obtained by extracting the aqueous solution three times with chloroform: yield, 2.6 g. (0.013 mole), 65%; m.p. 213–214° dec.; λ_{max} 285 mμ (ϵ 25,000).

Anal. Calcd. for $C_8H_9O_6N$: C, 44.65; H, 4.17. Found: C, 44.86; H, 4.55.

3,4-Dimethoxy-2,5-dicarbomethoxypyrrole (Ie).—The dihydroxypyrrole was etherified by suspending 150 mg. (0.7 mmole) in 5 ml. of ethanol to which was added a solution of freshly prepared diazomethane in ether. A slight excess of diazomethane was kept in the solution for 15 min. and the solvents were then removed under reduced pressure. The oily residue crystallized and melted at 49–72°. It was chromatographed from 5 g. of alumina and the main fraction came through with 30% benzene–ether and ether alone: yield, 80 mg. (0.327 mmoles), 47%; λ_{max} 272 mμ (ϵ 31,000). The material was recrystallized from ether and melted at 84–86°.

Anal. Calcd. for $C_{10}H_{13}O_6N$: C, 49.38; H, 5.35. Found: C, 49.50; H, 5.50.

2-Dimethylaminomethyl-3,4-diphenylpyrrole (III).—To a solution of 1.1 g. (5.2 mmoles) of 3,4-diphenylpyrrole dissolved in 50 ml. of methanol were added 550 mg. (5.7 mmoles) of potassium acetate, 410 mg. (5.5 mmoles) of 37% formaldehyde solution,

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(15) H. T. Clarke and E. E. Dreger "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 87.

(16) A. Ahlquist and T. Ekencranz, *Arkiv Kemi, Mineral. Geol.*, **13**, 265 (1908).

and 420 mg. (5.2 mmoles) of dimethylamine hydrochloride at 0° under an atmosphere of nitrogen. The reaction mixture was kept at this temperature for 12 hr. and most of the methanol was then removed under vacuum until the residue became cloudy. About 50 ml. of ether was added to the residue and the entire contents were placed into a separatory funnel and shaken with 50 ml. of 5 *N* HCl. The ether layer was separated and the aqueous layer was washed again with 50 ml. of ether. The aqueous layer was then made basic with 10% NaOH and extracted twice more with 50 ml. portions of ether. The ether was removed and the residue weighed 612 mg. (2.2 mmoles), 42.3%. A sample for analysis was sublimed at 100° (0.05 mm.)

Anal. Calcd. for $C_{19}H_{20}N_2$: C, 82.60; H, 7.25. Found: C, 82.38; H, 7.30.

Magnesium Octaphenylporphine (IV).—To 4.15 g. (0.0154 mole) of the Mannich base dissolved in 200 ml. of xylene was added 10 ml. of an ether solution of ethylmagnesium bromide (0.016 mole). The reaction mixture was refluxed for 20 hr. under an atmosphere of nitrogen. The cooled solution contained a blue-colored precipitate which was filtered off and extracted for 6 hr. from a thimble with a solution of 150 ml. of benzene containing 600 mg. of benzoquinone. The cooled extract was brown in color and a spectrum showed that it was nonporphyrin in nature. The material in the thimble was extracted for 12 hr. with a second solution of 200 mg. of benzoquinone in 100 ml. of benzene. The residue in the thimble consisted of bluish crystals and was recrystallized from hot dimethylformamide in small portions: yield, 1.7 g. (1.85 mmoles), 48.04%. The analytical results agree best for a molecular formula which contains one molecule of dimethylformamide.

Anal. Calcd. for $C_{68}H_{44}MgN_4 \cdot C_3H_7NO$ (1013): C, 84.11; H, 5.03; Mg, 2.37. Found: C, 84.06; H, 5.21; Mg, 2.58.

Octaphenylporphine (V).—Magnesium octaphenylporphine 80 mg. (0.083 mmole) was suspended in 80 ml. of glacial acetic acid and refluxed for 24 hr. under an atmosphere of nitrogen. The cooled acetic acid solution was neutralized with sodium carbonate and the microcrystalline blue powder was filtered off: yield, 41 mg. (0.043 mmole), 51.8%.

Anal. Calcd. for $C_{68}H_{46}N_4$ (918): C, 88.88; H, 5.01. Found: C, 88.50; H, 5.50.

Ferrioctaphenylporphine Acetate (VI).—To a solution of 800 mg. of ferrous chloride, 1 g. of ferric chloride, and 500 mg. of potassium acetate in 200 ml. of glacial acetic acid was added 200 mg. (0.206 mmole) of powdered magnesium octaphenylporphine. The reaction mixture was refluxed under an atmosphere of nitrogen for 18 hr. The cooled solution was filtered and the ferric octaphenylporphine acetate was recrystallized in small portions from hot dimethylformamide: yield, 68 mg. (0.68 mmole), 33.01%. The analytical results agree best with a ferrioctaphenylporphine acetate structure.

Anal. Calcd. for $C_{70}H_{47}FeN_4O_2$ (1031): C, 81.48; H, 4.56; Fe, 5.43. Found: C, 81.91; H, 4.90; Fe, 5.12.

2-Dimethylamino-3,4-di(*p*-methoxyphenyl)pyrrole (IIIa).—Into a 250-ml. three-necked flask was placed 190 ml. of dry methanol, 2 g. (7.17 mmoles) of 3,4-di-*p*-methoxyphenylpyrrole, and 703 mg. (7.17 mmoles) of potassium acetate. The flask was placed in an ice bath and cooled down to 5°. To the cooled solution were then added 581 mg. (7.17 mmoles) of 37% formaldehyde solution and 647 mg. (7.89 mmoles) of dimethylamine hydrochloride. The reaction mixture was stirred for 6 hr. under an atmosphere of nitrogen at 5–10°. At the end of this time the stoppered flask was placed in the cooler and kept there for 24 hr. Most of the methanol was then removed under vacuum and about 75 ml. of ether was added to the residue. The entire contents were placed in a separatory funnel and shaken with 60 ml. of 5 *N* HCl. The layers were separated and the aqueous layer was washed with another 75 ml. of ether. The combined ether layers were neutralized with sodium bicarbonate solution, washed with water, and dried with magnesium sulfate for 1 hr. The ether was removed under vacuum leaving behind a residue which on sublimation turned out to be starting material weighing 0.65 g. (2.35 mmoles, 33%). The acidic aqueous layer was neutralized with 10% NaOH solution and extracted with three 100-ml. portions of ether. The combined ether layers were washed with water, and dried with magnesium sulfate. The ether was removed under vacuum leaving behind a fluffy precipitate which melted at 56–59°: yield, 0.40 g. (1.19 mmoles), 25%. The Mannich base was not further purified but used directly in the porphyrin synthesis.

Anal. Calcd. for $C_{21}H_{24}N_2O_2$: N, 8.33. Found: N, 8.46.

Magnesium Octa(*p*-methoxyphenyl)porphine (IVa).—Into a 50-ml. three-necked flask equipped with a reflux condenser and nitrogen inlet were placed 350 mg. (1.06 mmoles) of 2-dimethylamino-3,4-di(*p*-methoxyphenyl)pyrrole and 30 ml. of dry xylene. To this solution was added 6 ml. (1.20 mmoles) of an ether solution of ethylmagnesium bromide under an atmosphere of dry nitrogen. The reaction mixture was then refluxed for 24 hr. with stirring. The cooled solution was evaporated to half its volume under vacuum and the precipitate in the flask was filtered off and air-dried. The blue powder was placed in a thimble and extracted with benzene in a micro-Soxhlet extractor for 48 hr. until the extract was colorless. The blue residue in the thimble weighed 260 mg. (0.228 mmole), 87.7% of crude product. The benzene extract contained no porphyrin material as evidenced by a spectral examination. The magnesium complex was rather insoluble in most organic solvents but readily dissolved in hot dimethylformamide and hot pyridine from which it was recrystallized in microcrystalline form. An attempt to recrystallize it from hot dimethylformamide gave similar results.

Anal. Calcd. for $C_{76}H_{60}MgN_4O_8$ (1180): N, 4.75. Found: N, 5.03.

Octa(*p*-methoxyphenyl)porphine (Va).—A suspension of 60 mg. (0.052 mmole) of the magnesium octa(*p*-methoxyphenyl)porphine in 300 ml. of glacial acetic acid was refluxed for a period of 48 hr. under an atmosphere of nitrogen. The cooled acetic acid solution was neutralized with solid sodium carbonate and the precipitated porphyrin was filtered off, washed with water, methanol, and a small amount of ether, and dried in the desiccator: yield, 45 mg. (0.040 mmole), 77.0%. For analysis the compound was dried in high vacuum at 150° for 48 hr.

Anal. Calcd. for $C_{76}H_{62}N_4O_8$ (1158): C, 78.75; H, 5.36; N, 4.84. Found: C, 78.48; H, 5.70; N, 4.82.

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