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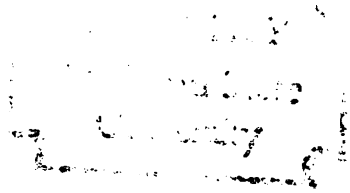

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thesis entitled

THE SYNTHESIS OF 5,15-BIS(3,5-DINITROPHENYL)-2,3,7,8,12,13,17,18-OCTAMETHYLPORPHYRIN

presented by

Robert V. Honeychuck

has been accepted towards fulfillment
of the requirements for
M.S. degree in Chemistry

Chi K. Chang
Major professor

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THE SYNTHESIS OF 5, 15-BIS(3,5-DINITROPHENYL) 2,3,7,8,12,13,17,18-OCTAMETHYLPORPHYRIN

by

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ABSTRACT

THE SYNTHESIS OF 5,15-BIS(3,5-DINITROPHENYL)-
2,3,7,8,12,13,17,18-OCTAMETHYLPORPHYRIN

By

Robert V. Honeychuck

The title compound was synthesized from 2-benzyloxycarbonyl-3,4,5-trimethylpyrrole and 3,5-dinitrobenzoyl chloride. The route involved condensation of a 5,5'-free dipyrromethane with 3,5-dinitrobenzaldehyde in methanol with a catalytic amount of p-toluenesulfonic acid. Condensation in propionic acid produced the corresponding monoaryl compound.

To Nancy, whose infinite patience and understanding

made this work possible.

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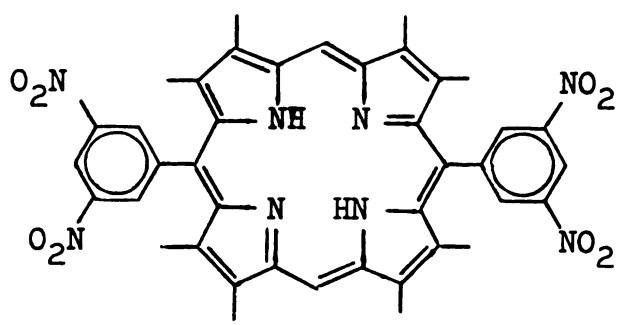
INTRODUCTION

A considerable amount of work has been done in recent years on porphyrins coupled to other molecules. These elaborated porphyrins when metalated serve as models of hemoglobin[1], myoglobin[1,5], enzymes with two metal ions held in close proximity at the active site[2,4,17], and cytochromes P-450[3]. As a precursor to a porphyrin which could be coupled simultaneously on both sides of the prophyrin plane, the meso-diaryl compound 5,15-bis(3,5-dinitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (1) was synthesized.



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Several routes to meso-diaryl porphyrins have already been published. Baldwin and coworkers[6] attached two benzaldehyde moieties to a strap and condensed them with benzyl 3,4-dimethylpyrrole-2-carboxylate

to give a bis dipyrromethane. After catalytic hydrogenolysis and cyclization with trimethyl orthoformate a strapped porphyrin, with the strap stretching from one meso-aryl group to the other, was obtained. Several diaryloctaethylporphyrins (diaryl OEP's) have been made by Ogoshi, et. al.[7] Various benzaldehyde derivatives were combined with 3,3'4,4'-tetraethyl-2,2'-dipyrrylmethane in benzene with trifluoroacetic acid yielding 5,15-diaryl-2,3,7,8,12,13,17,18-octaethylporphyrins. In this study a change in solvent to propionic acid gave monoaryl OEP's in 15-25% yield.

Gunter and Mander[8] have reported that the reaction of 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane with o-nitrobenzaldehyde in methanol with a catalytic amount of p-toluenesulfonic acid gave, after oxidation, 5,15-bis(o-nitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin. This approach was used in this work (Figure 1) because the procedure promised a high yield porphyrin synthesis under mild conditions.

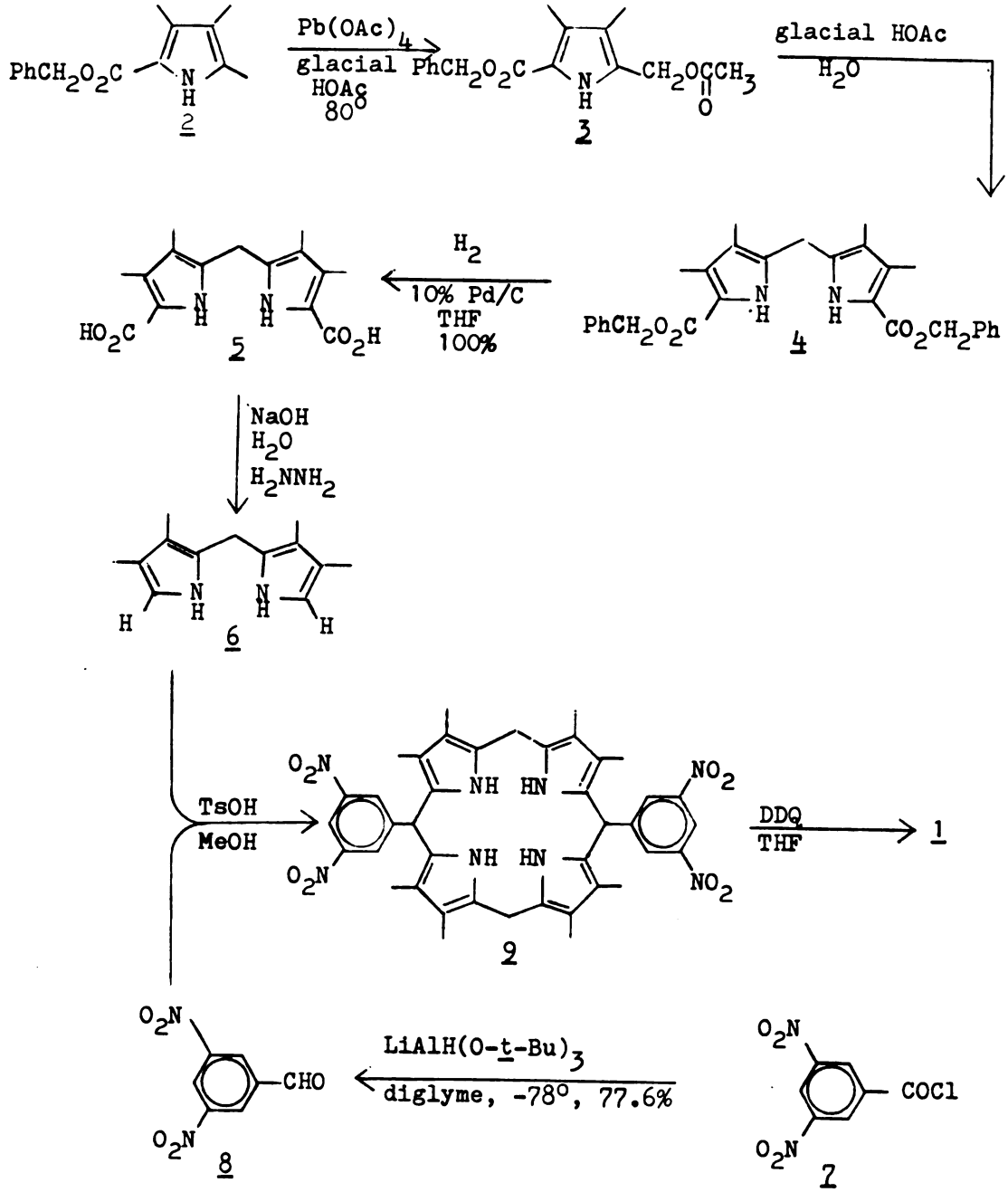

Figure 1. Synthesis of 5,15-bis(3,5-dinitrophenyl)-2,3,7,8,12,13,17, 18-octamethylporphyrin (1).

RESULTS AND DISCUSSION

The lead tetraacetate method of Siedel and Winkler[9] was used to convert α-methylpyrrole 2 to α-acetoxymethylpyrrole 3. This is a clean reaction which proceeds in high yield in 10 minutes, and is conveniently monitored by thin layer chromatography (TLC). Solvolysis to the symmetrical dipyrromethane 4 was accomplished in aqueous acetic acid[11]. Bromine vapor is easily used here to develop TLC plates[11b]. Dipyrromethanes oxidize to the red dipyrromethenes immediately; pyrroles turn yellow temporarily.

The benzyl groups of dipyrromethane 4 were removed by catalytic hydrogenolysis with 10% palladium on carbon. An acid or base hydrolysis is not preferred here since under these conditions decarboxylation is enhanced. The major problem usually encountered in a hydrogenolysis of a dipyrromethane is precipitation of the product, which is then difficult to wash away from the catalyst. The best procedure involves use of a small amount of catalyst. Some extra product may be obtained by washing the catalyst with methanol or tetrahydrofuran (THF), but this is not always effective. Hot wash solvents are to be avoided since they decarboxylate the product.

Dipyrromethane-5,5'-dicarboxylic acid 5 was decarboxylated in aqueous hydroxide with hydrazine stabilizer under high pressure and temperature. The recommended[8] procedure in a sealed Pyrex tube at 170°C resulted in an explosion. A steel reaction tube gave satisfactory

results. Many problems were encountered in the decarboxylation of this diacid; Paine[12] has presented a discussion of these difficulties. Decarboxylation in the following solvents failed, due either to acid-catalyzed rearrangements or lack of decarboxylation: trifluoroacetic acid, benzene + trifluoroacetic acid, dimethyl formamide, sodium hydroxide + methanol, sodium hydroxide + water, and sodium hydroxide + diglyme (diethylene glycol dimethyl ether).

Lithium aluminum tri-tert-butoxy hydride was prepared[13,14,15] from lithium aluminum hydride and 3 equivalents of t-butyl alcohol in ethyl ether. The dry powdered product was dissolved in diglyme for the subsequent reduction. Direct preparation of this hydride in diglyme[14] failed.

The procedure of Siggins, et. al.[13], was used in the hindered hydride reduction of 3,5-dinitrobenzoyl chloride (7) to 3,5-dinitrobenzaldehyde (8). Over-reduction to the alcohol occurs if too much of the unhindered species (lithium aluminum hydride, lithium aluminum t-butoxy hydride, lithium aluminum di-t-butoxy hydride) is present. Lithium aluminum tri-t-butoxy hydride is a white powder when pure, but gray when contaminated with the other hydrides.

Condensation of 3,5-dinitrobenzaldehyde (8) and 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane (6) took place in methanol with a catalytic amount of p-toluenesulfonic acid, giving the brown porphyrinogen 9 in 33% yield from 6. The 250 MHz proton nmr of 9 (Figure 2) indicates that it is present as a mixture of cis and trans isomers (phenyls cis or trans to each other). The presence of 4 distinct methyl singlets in the δ1.6-2.0 region supports this conclusion. Also, the porphyrinogen produced is the diaryl species, not monoaryl. Peaks C and D are the cis

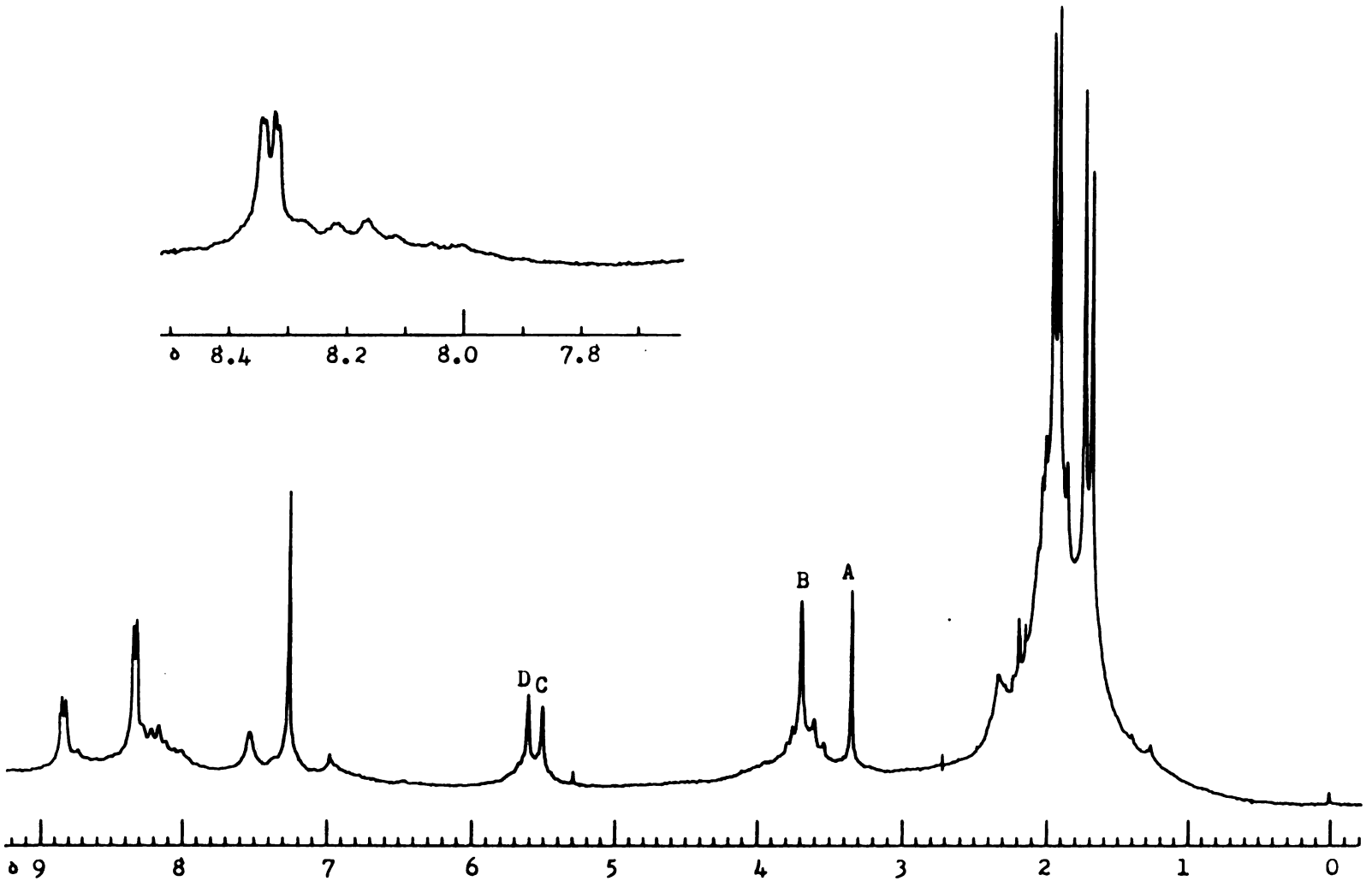

Figure 2. 250 MHz ^{1}H nmr of porphyrinogen 9.

or trans benzylic protons. The monoaryl compound can have only a single peak here for its single benzylic proton. For the area ratios (A and B are the $-CH_2-$ protons):

$$\frac{C + D}{A + B} = 0.533$$

This is close (6.7% error) to the expected value of 0.500 in the diaryl compound. In any case, the best evidence is that the porphyrin made from 9 is clearly diaryl and not monoaryl.

Gunter and Mander have shown[8] that no mass spectrum could be obtained with bis(o-nitrophenyl)-octamethylporphyrinogen. Consistent with this, 9 did not give a mass spectrum.

When dipyrromethane 6 was condensed with 3,5-dinitrobenzaldehyde in propionic acid, the monoaryl porphyrin resulted, in agreement with Ogoshi, et. al.[7]. This could occur[8,16] by acid-catalyzed rearrangement of the porphyrinogen precursors as shown in Figure 3.

The proton nmr of 10 is presented in Figures 4, 5, and 6. These spectra were taken in the following manner:

Figure 4 (96:3:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4Si$)

↓ Wash with 5% aq $NaHCO_3$

Figure 5 (98:1:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4Si$)

↓ Wash with 5% aq $NaHCO_3$

Figure 6 (No F_3CCO_2H)

Figures 4 and 5 take advantage of the concentration dependent shift (δ8.6 to δ7.4) of trifluoroacetic acid to show no hidden peaks beneath the large TFA peak. The 10 assignments are made in Figure 4. Note that

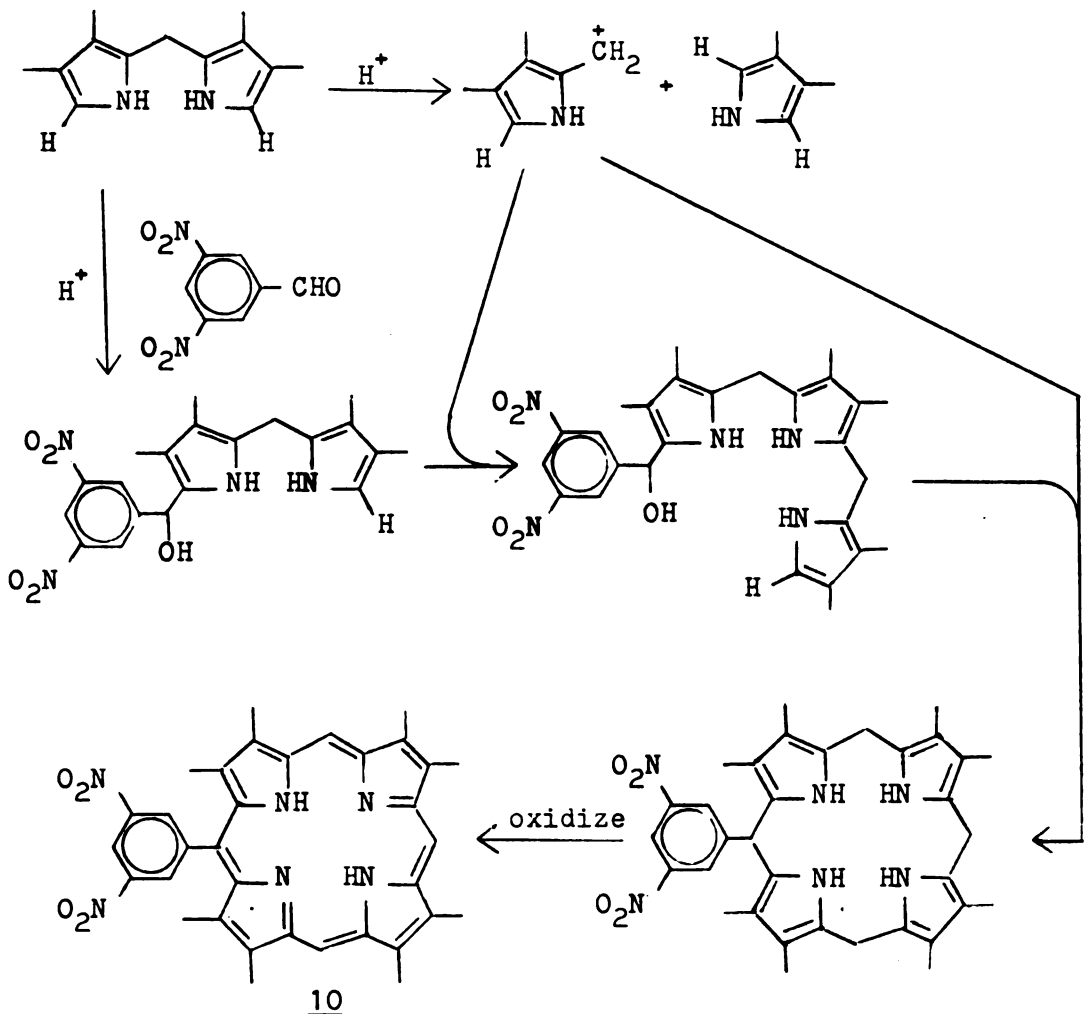

Figure 3. Possible pathway for the production of monoaryl porphyrin 10.

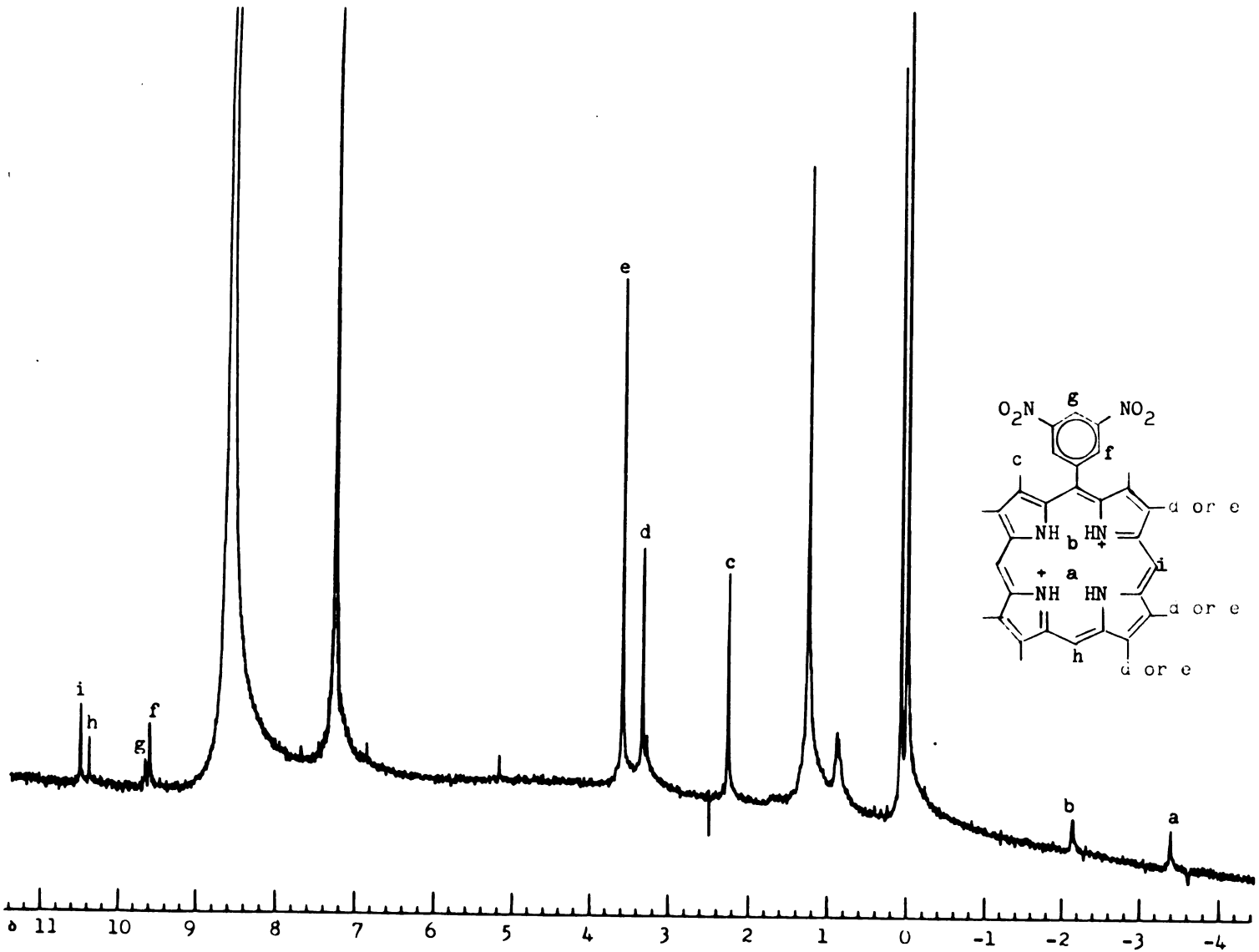

Figure 4. 250 MHz ^{1}H nmr of monoaryl porphyrin 10 in 96:3:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4Si$.

Table 1. Printout of Figure 4.

#	[illegible]	[illegible]	[illegible]	INTEGRAL	[illegible]
1	911	2623.511	10.4534	2.317	3.37[illegible]
2	1019	2599.[illegible]09	10.3642	2.476	2.90[illegible]
3	1[illegible]24	[illegible]	4.7[illegible]4[illegible]	2.133	[illegible]
4	1[illegible]	[illegible]1	4.7[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	[illegible].44[illegible]	[illegible]33	[illegible]
19	[illegible]	[illegible]	.44[illegible]	[illegible]	[illegible]
20	[illegible]	2110.[illegible]44	[illegible].4[illegible]	2.13[illegible]	3.1[illegible]4
21	[illegible]	210[illegible].[illegible]1	[illegible].4[illegible]4[illegible]	2.0[illegible]2	3.[illegible]
22	2[illegible]	2104.542	3.4136	.903	4.[illegible]34
23	2804	2102.262	3.4070	1.444	4.725
24	2811	2101.023	3.3996	.833	4.537
25	2817	2099.506	3.3935	.867	4.330
26	2821	2097.350	3.3854	.573	4.442
27	2826	2096.913	3.3831	.828	4.332
28	2831	2095.454	3.3773	1.309	4.317
29	2842	2092.630	3.3650	1.923	4.213
30	2851	2090.094	3.3559	.523	4.0[illegible]3
31	2855	2088.846	3.3511	.784	4.120
32	2860	2087.579	3.3455	1.340	4.032
33	2870	2084.883	3.3350	.754	3.923
34	2875	2083.380	3.3290	1.733	3.939
35	2889	2079.921	3.3152	1.015	3.314
36	2893	2078.533	3.3097	.373	3.[illegible]30
37	2898	2077.132	3.3041	.725	3.[illegible]3
38	2903	2075.565	3.2990	1.003	3.[illegible]31
39	2909	2074.069	3.2913	1.104	3.543
40	2917	2071.507	3.2863	.331	3.3[illegible]
41	2922	2070.637	3.2731	.563	3.339
42	2926	2069.378	3.2730	1.030	3.337
43	2934	2067.249	3.2645	.404	3.4[illegible]
44	2933	2066.054	3.2599	1.211	3.3[illegible]
160	7191	996.712	3.5944	12.311	12.3[illegible]
161	7227	987.055	3.5463	.326	2.63
162	7231	975.873	3.5416	1.039	2.64[illegible]
163	7424	932.762	3.3293	5.739	5.709
164	7466	921.103	3.2826	.532	2.345
165	7475	918.745	3.2732	2.134	3.034
166	8406	762.878	2.2503	5.474	5.413
167	9262	[illegible].[illegible]2[illegible]	1.3044	1.235	2.722
168	9[illegible]	[illegible].174	1.3040	.5[illegible]	3.0[illegible]

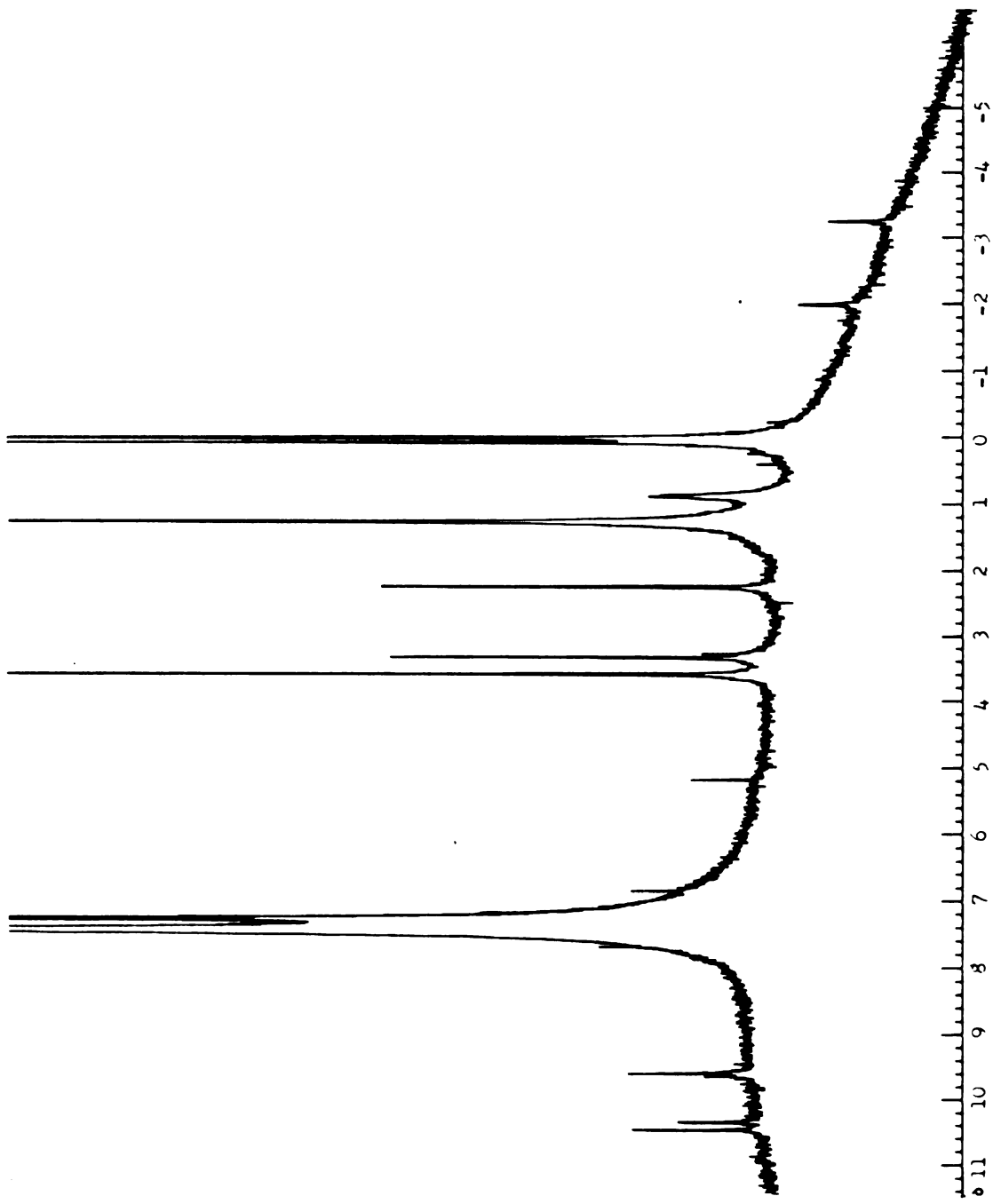

Figure 5. 250 MHz ^1H nmr of monoaryl porphyrin 10 in 98:1:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4Si$.

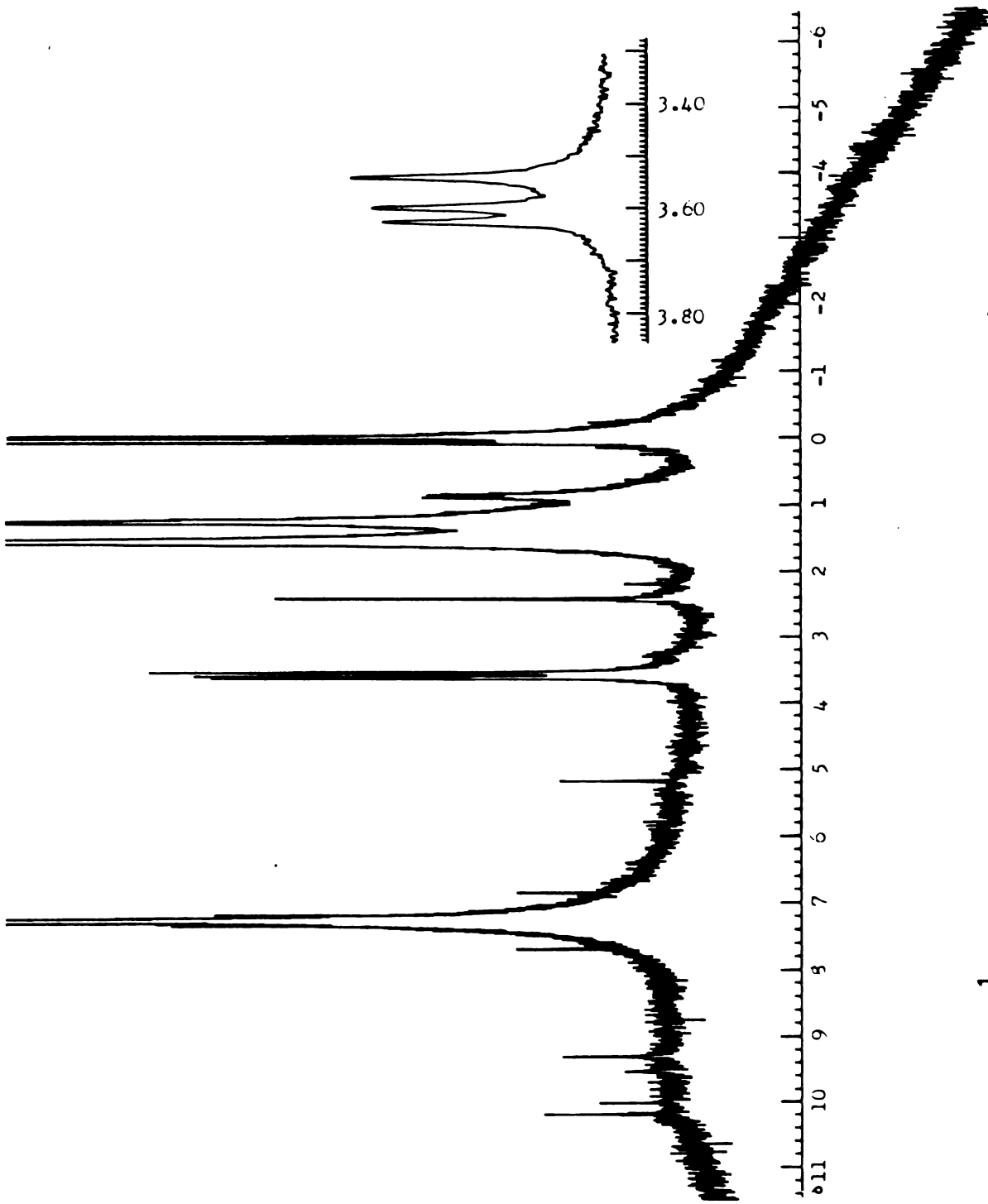

Figure 6. 250 MHz ^1H nmr of monoaryl porphyrin 10 in 99:1 $CDCl_3$:$(CH_3)_4Si$.

the c methyls appear more than 1 ppm upfield of the other methyls due to shielding by the phenyl ring. The b protons reside on the nitrogens with lower electron density, presumably those closer to the nitro groups.

The e methyls in Figures 4 and 5 are present as a single sharp peak. When acid is removed (Figure 6), e splits into two singlets, as might be predicted for a first order spectrum of 10. Interpretation of Figures 4 and 5 as a 1:1 mixture of diarylporphyrin 1 and octamethyl porphyrin is thus ruled out. This mixture could not possibly give the pattern in Figure 6.

These spectra are typical of many porphyrins in that all impurities are greatly magnified. Many porphyrins are so insoluble that a reasonable spectrum can be obtained only on a pulsed Fourier transform instrument. Figures 4, 5, and 6 are the result of 502, 1021, and 1000 scans, respectively. They all show stopcock grease[23] at δ0.1, 0.9, and 1.2, methylene chloride at δ5.2, and chloroform at δ7.2.

Porphyrinogen 9 was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in tetrahydrofuran to give the diaryl octamethyl porphyrin 1. Comparison of the nmr spectra of 10 and 1 (Figures 4-7) shows that in this case the diaryl compound was obtained. Two methyl singlets are seen in place of 3 or 4 for monoaryl porphyrin 10 and one meso peak instead of two. The printout for Figure 7 is given in Table 2.

Several conclusions may be drawn from this work regarding the synthesis of 5,15-diarylporphyrins. First, the decarboxylation of 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane-5,5'-dicarboxylic acid and similar dipyrrylmethanes must be done under basic conditions to avoid acid-catalyzed rearrangements. Second, the porphyrin must be checked

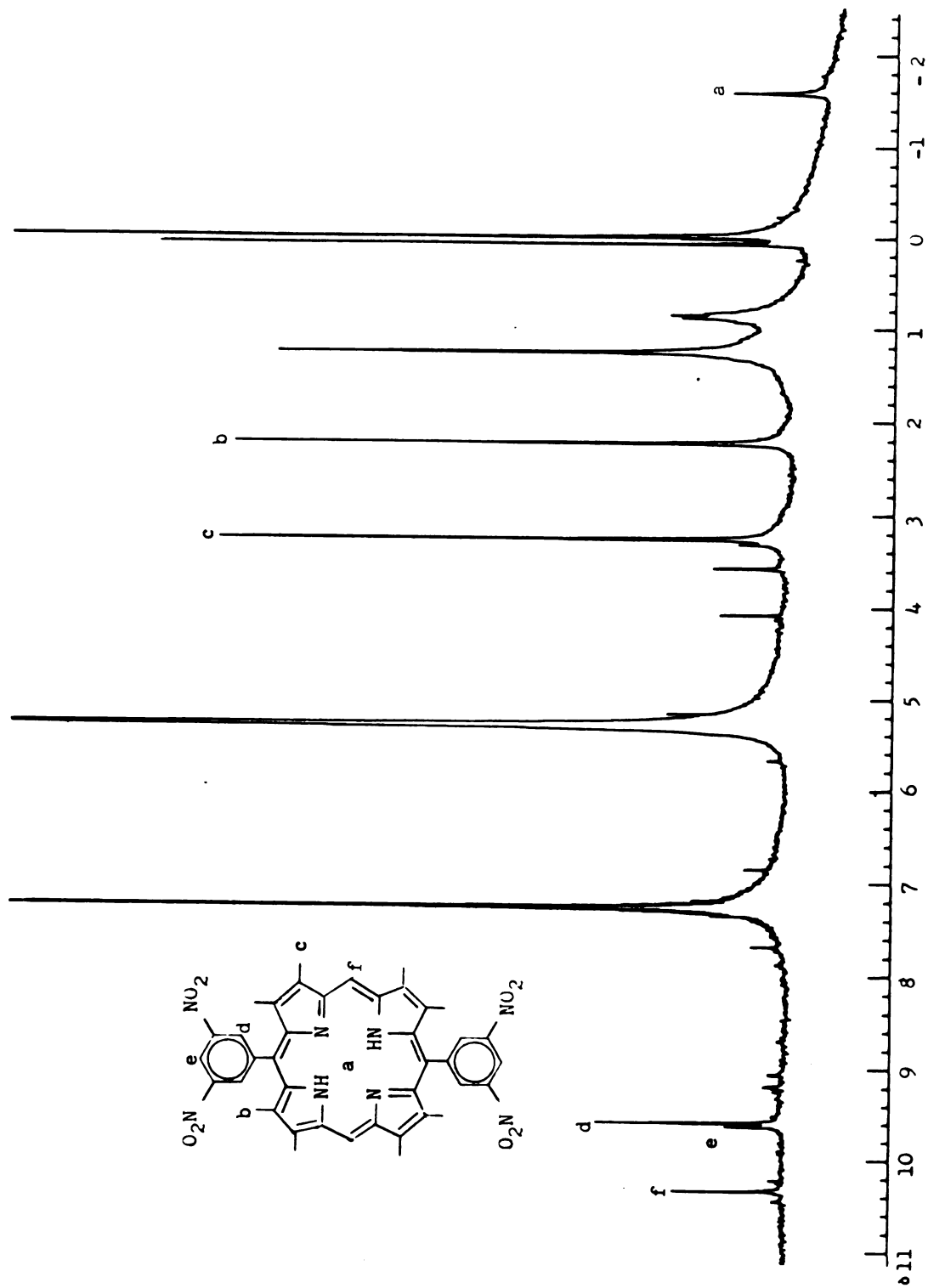

Figure 7. 250 MHz ^1H nmr of diaryl porphyrin 1.

Table 2. Printout of Figure 7.

#	CH. NO	FREQ	PPM	INTEGRAL	INTENSITY
1	1050	2584.839	10.3335	1.035	3.999
2	1731	2397.773	9.5359	.934	5.575
3	1738	2395.764	9.5779	1.264	4.465
4	3788	1842.101	7.3245	.245	3.393
5	3792	1830.982	7.3200	.254	3.556
6	3796	1829.992	7.3156	.264	3.720
7	3800	1828.778	7.3112	.268	3.796
8	3804	1827.673	7.3058	.276	3.90[illegible]
35	5635	1324.340	5.2945	27.856	19.363
40	7486	815.460	3.2601	5.334	15.400
41	8422	558.045	2.2312	6.013	13.109
42	9311	313.592	1.2541	3.602	12.245
43	9359	300.344	1.2004	2.221	3.526
44	9651	220.122	.8800	2.056	3.955
45	96[illegible]	213.200	.8523	1.3[illegible]	4.1[illegible]

carefully by spectroscopic methods to show that the diaryl (not the monoaryl) product has indeed been produced. The appearance of the correct molecular ion in the mass spectrum is helpful in this respect but cannot be expected in every case since these diaryl porphyrins often do not melt at the maximum possible temperature of a particular spectrometer. Finally, although in one case[8] high yield procedures have been reported, the method may not be generally useful since here a low yield was obtained in the final oxidation step, and the overall yield (1.40%) is low.

EXPERIMENTAL

General

NMR spectra were obtained on a Varian T-60 or on a Bruker WM-250 instrument with tetramethylsilane as internal standard. Mass spectra were done on a Finnigan 4021 with INCOS data system. Infrared spectra were recorded on a Perkin-Elmer 283-B spectrometer. UV-visible spectra were taken on a Varian Cary 219 machine with 1 cm quartz cells. Melting points are uncorrected.

5-Acetoxymethyl-2-benzyloxycarbonyl-3,4-dimethylpyrrole (3)

To a 3-necked 2 liter round-bottomed flask with a condenser was added 60.8 g (0.250 mol) of α-methylpyrrole 2, 500 ml of glacial acetic acid, and 133 g (0.300 mol) of lead tetraacetate. The solution was heated on a steam bath at 80° for 10 min, poured into a beaker, and diluted with 500 ml of water. The precipitate was filtered and washed with water and a portion dried on the vacuum pump giving a light yellow solid: nmr ($CDCl_3$) δ 1.96 (s, 3H), 2.00 (s, 3H), 2.23 (s, 3H), 4.92 (s, 2H), 5.20 (s, 2H), 7.25 (s, 5H); mass spectrum m/e (rel. inten.) 91 (100), 301 (20, molecular ion); IR (KBr) 1240, 1278, 1500, 1673, 1735, 3310 cm^{-1}; mp 102-105°. This melting point has been previously reported as 118-120°[18] and 169-171°[19].

5,5'-Bis(benzyloxycarbonyl)-3,3',4,4'-tetramethyl-2,2'-dipyrromethane (4)

Pyrrole 3 (75.2 g, 0.250 mol) and glacial acetic acid (2700 ml) were added to a 3-necked 5 liter round-bottomed flask with a condenser. The flask was heated with a steam bath and 700 ml of water was added after the pyrrole went into solution. If the pyrrole is added to aqueous acetic acid, it dissolves very sluggishly. The dark solution was heated for 2 hours and diluted with 1000 ml of water. The product was filtered and washed with 4 liters of water and 500 ml of 20:80 acetone:water and dried on a vacuum pump giving yellow crystals: yield 45.6 g (77.6%); nmr ($CDCl_3$) δ1.90 (s, 6H), 2.20 (s, 6H), 3.66 (s, 2H), 5.09 (s, 4H), 7.10 (s, 10H), 9.4 (br s, 2H); mass spectrum m/e (rel. inten.) 91 (100), 470 (51, molecular ion); IR (KBr) 1270, 1442, 1500, 1645, 1682, 3352 cm^{-1}; mp 174-175°; lit. mp^{20} 179°.

3,3',4,4'-Tetramethyl-2,2'-dipyrromethane-5,5'-dicarboxylic acid (5)

To a 100 ml 1-necked round-bottomed flask with a magnetic stirring bar on a one atmosphere hydrogenation apparatus were added 2.40 g (0.00510 mol) of dipyrromethane dibenzyl ester 4 and 50 ml of tetrahydrofuran. After the starting material dissolved, 0.203 g of 10% palladium on carbon was added and the flask was evacuated and filled with hydrogen three times. The hydrogenolysis was complete in 8 hrs, using 260 ml (0.0106 mol) of hydrogen. The catalyst was filtered on a Büchner funnel, washed with 500 ml of THF, dried, and weighed to determine whether any product remained on it. (A visual inspection will suffice at this point since palladium on carbon is gray when contaminated with 5 and black when uncontaminated.) The filtrate was filtered

5 more times to remove residual catalyst and evaporated on the rotary evaporator. The white solid was dried on the vacuum pump: yield 1.48 g (100%); nmr (DMSO-d_6) δ1.86 (s, 6H), 2.07 (s, 6H), 3.63 (s, 2H), 10.7 (br s, NH); lit.[21] nmr (DMSO-d_6) δ1.89 (s, 6H), 2.14 (s, 6H), 3.72 (s, 2H), 10.96 (s, NH); mass spectrum m/e (rel. inten.) 44 (54), 152 (18), 290 (13, molecular ion); IR (KBr) 864, 1435, 3000-3400 cm^{-1}; mp 164° dec.

3,3',4,4'-Tetramethyl-2,2'-dipyrromethane (6)[22]

In a 75 ml steel reaction tube were placed 1.00 g (3.45×10^{-3} mol) of dipyrromethane dicarboxylic acid 5, 6.9 ml of 10% w/w aqueous sodium hydroxide solution, and 0.10 ml of hydrazine hydrate (containing 2.1×10^{-3} mol of hydrazine). Nitrogen was bubbled through the solution for 10 minutes and the tube was sealed and heated at 170°C in an oil bath for 4 hrs. The vessel was chilled to 0° and opened and the tan product removed with water. The base was neutralized with sulfur dioxide and the product filtered, washed with cold water, dried, and weighed: yield 0.519 g (74.5%). The product was used immediately in the condensation with 3,5-dinitrobenzaldehyde.

Preparation of lithium aluminum tri-t-butoxyhydride in ethyl ether[14,15]

All of the glassware in this reaction was oven dried and kept under dry nitrogen. A 3-necked 2 liter round-bottomed flask was equipped with an overhead stirrer, condenser, and 250 ml addition funnel. Ethyl ether (480 ml) and lithium aluminum hydride (7.28 g, 0.192 mol) were placed in the flask. A solution of 44.6 g (0.604 mol) of t-butyl alcohol in 150 ml of ethyl ether was added through the addition funnel over 2 hrs. The

suspension was stirred another 30 minutes, at which time slow evolution of hydrogen still occurred. The solvent was decanted, leaving a gray solid. The solid was dried on the vacuum pump with a heat gun. The dried solid was light gray, but weighed only 37.5 g, not the desired 48.8 g. Accordingly, 480 ml of ethyl ether was added along with 22.3 g (0.302 mol) of t-butyl alcohol in 100 ml of ethyl ether. The suspension was stirred under nitrogen for 19 hrs. At the end of 19 hrs, the suspension still evolved hydrogen very slowly. Decantation and drying gave a light gray solid which when dissolved in diethylene glycol dimethyl ether (diglyme) satisfactorily reduced 3,5-dinitrobenzoyl chloride to the corresponding aldehyde.

Attempted preparation of lithium aluminum tri-t-butoxyhydride in diglyme[14]

To a dry 3-necked 200 ml round-bottomed flask under dry nitrogen with a magnetic stirring bar and addition funnel were added 1.82 g (0.0480 mol) of lithium aluminum hydride and 40 ml of dried diglyme. Tert-butyl alcohol (13.4 ml, 0.143 mol) was added over 1 hr through the addition funnel. The flask was stirred for 2 more hours. The resulting gray suspension was filtered through a fritted glass funnel under nitrogen. Much gray material was filtered out, and the filtrate did not reduce 3,5-dinitrobenzoyl chloride to the aldehyde.

3,5-Dinitrobenzaldehyde (8)[13]

A diglyme solution of lithium aluminum tri-t-butoxy hydride was prepared in the following way. To an Erlenmeyer flask was added 11.6 g (0.0456 mol) of the hydride and 40 ml of dry diglyme. The flask was stoppered and stirred overnight. The gray suspension was filtered the

next day through a fritted glass funnel, pushed by dry nitrogen, through Celite 545, directly into the addition funnel used in the reduction step. The resulting solution was nearly clear and light gray.

The reduction took place as follows. To a 3-necked 250 ml round-bottomed flask with an overhead stirrer, the above addition funnel, and the exit bubbler, was added 9.59 g (0.0414 mol) of 3,5-dinitrobenzoyl chloride and 40 ml of dry diglyme. The entire reaction was done under nitrogen. After the acid chloride went into solution, the flask was placed in a dry ice-isopropyl alcohol bath and cooled for several minutes. The reducing agent was added through the addition funnel over 70 min. The reaction mixture turned red on addition of the hydride. Stirring continued for 30 more minutes.

The cold reaction mixture was poured with stirring into a 400 ml beaker containing 13 ml of concentrated hydrochloric acid, 26 ml of saturated aqueous sodium chloride, and 13 g of crushed ice. An additional 13 ml of saturated aqueous sodium chloride was added and a brown upper layer formed. The contents were transferred to a separatory funnel and the upper layer was reserved while the bottom was extracted with three 100 ml portions of benzene. The upper layer and the benzene extracts were combined and washed with seven 300 ml portions of 0.12 M aqueous hydrochloric acid. Two 125 ml portions of aqueous 2% sodium bicarbonate neutralized remaining acid in the benzene layer; the pH of the second washing was 8. The organic layer was dried overnight over anhydrous sodium sulfate, filtered, and reduced on the rotary evaporator to dryness. The product was dried on the vacuum pump to give 3,5-dinitrobenzaldehyde as a tan solid yield 6.30 g (77.6%); nmr ($CDCl_3$)

δ8.88 (d, 2H), 9.11 (t, 1H), 10.01 (s, 1H); mass spectrum m/e (rel. inten.) 195 (100), 196 (79, molecular ion); IR ($CHCl_3$) 1348, 1555, 1721 cm^{-1}; mp 74-78°. A portion recrystallized from toluene/hexanes gave a melting point of 76-78°.

5,15-Bis(3,5-dinitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrinogen (9)

In a 1-necked 100 ml round-bottomed flask were placed 0.611 g (3.02×10^{-3} mol) of 5,5'-free dipyrromethane 6, 0.592 g (3.02×10^{-3} mol) of 3,5-dinitrobenzaldehyde, 0.143 g (7.55×10^{-4} mol) of p-toluenesulfonic acid monohydrate, and 35 ml of methanol. The flask was stoppered and left for 12 hrs. Filtration of the reaction mixture on a fine fritted glass funnel gave brown crystals which were washed with ice cold methanol, pumped dry, and stored in the dark under nitrogen at 0°. The product was obtained as a mixture of cis and trans isomers: yield 0.377 g (32.9%); nmr ($CDCl_3$) δ1.68 (s, 12H, CH_3), 1.74 (s, 12H, CH_3), 1.92 (s, 12H, CH_3), 1.96 (s, 12H, CH_3), 3.34 (s, 4H, CH_2), 3.7 (m, 4H, CH_2), 5.50 (s, 2H, CH), 5.60 (s, 2H, CH), 7.5 (br s, NH), 8.32 (d, 4H, ArH_2), 8.34 (d, 4H, ArH_2), 8.8 (m, 4H, O_2N-C-CH-C-NO_2). This material does not melt but turns black gradually from 150-300°C; thus, no mass spectrum could be obtained.

5-(3,5-Dinitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (10)

In a 500 ml 1-necked round-bottomed flask was placed 6.56 g (0.0226 mol) of dipyrromethane dicarboxylic acid 5. The flask was fitted with a septum and filled with nitrogen and 10 ml of trifluoroacetic acid was added via syringe. After 3 min the trifluoroacetic acid was collected

in a vacuum pump trap, leaving behind a red oil. The oil was transferred to a 1000 ml 1-necked round-bottomed flask and a solution of 3.63 g (1.85×10^{-2} mol) of 3,5-dinitrobenzaldehyde in 500 ml of propionic acid was added. The magnetically stirred flask was heated under reflux open to the air for 24 hrs. Solvent was evaporated with heat and an air line, giving a black tar. A portion of the tar was chromatographed on a silica gel preparative TLC plate with toluene. The first band near the solvent front was collected giving 10 as a brown solid: yield 0.0030 g (0.055%); nmr (96:3:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4Si$) δ 3.40 (s, 2H), -2.10 (s, 2H), 2.25 (s, 6H), 3.33 (s, 6H), 3.58 (s, 12H), 9.59 (s, 2H), 9.61 (s, 1H), 10.37 (s, 1H), 10.49 (s, 2H); nmr (99:1 $CDCl_3$:$(CH_3)_4Si$) δ2.41 (s, 6H), 3.54 (s, 6H), 3.60 (s, 6H), 3.62 (s, 6H), 9.30 (s, 2H), 9.53 (s, 1H), 10.01 (s, 1H), 10.18 (s, 2H); λ_{max} (CH_2Cl_2) nm 396 (Soret), 506, 541, 573, 626. This compound does not melt at less than 400°C and therefore gave no mass spectrum.

5,15-Bis(3,5-dinitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (1)

Porphyrinogen 9 (0.377 g, 4.96×10^{-4} mol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.449 g, 1.98×10^{-3} mol), and tetrahydrofuran (40 ml) were placed in a 100 ml 1-necked round-bottomed flask. The flask was stoppered, left at room temperature for 3 hrs, and put in the freezer for 30 min. Filtration on a fine fritted glass funnel (funnel A) gave a black solid containing some product. The solid was dissolved in methylene chloride and passed through a silica gel pad on another funnel (funnel B) giving a red filtrate. The filtrate from funnel A was reduced to dryness on the rotary evaporator and the solid transferred to a funnel (funnel C), where it was rinsed with 2 liters of

10% aqueous sodium hydroxide, removing the hydroquinone of DDQ. The aqueous filtrate at the end of the 2 liters was faint yellow. The material on funnel C was then rinsed with distilled water, dissolved in methylene chloride, and passed through another silica gel pad (funnel D). The filtrates from funnels B and D were reduced to dryness on the rotary evaporator. The solids were combined and dried on the vacuum pump giving 1 as a purple solid: yield 0.0310 g (8.29%); $\lambda_{max}(CH_2Cl_2)$ nm (ε) 395 (9.07×10^4), 512 (1.04×10^4), 546 (5.53×10^3), 578 (5.32×10^3), 630 (2.26×10^3); IR (KBr) 1340, 1545 cm^{-1}. A portion of the solid was further purified on a silica gel preparative TLC plate with CH_2Cl_2/CH_3OH and gave the following nmr (95:4:1 $CDCl_3$:F_3CCO_2H:$(CH_3)_4$-Si): δ-1.60 (s, 4H), 2.23 (s, 12H), 3.26 (s, 12H), 9.59 (s, 4H), 9.61 (s, 2H), 10.33 (s, 2H). The product does not melt below 400°C and gave no mass spectrum.

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