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PORPHYRIN SYNTHESIS FROM NITROCOMPOUNDS

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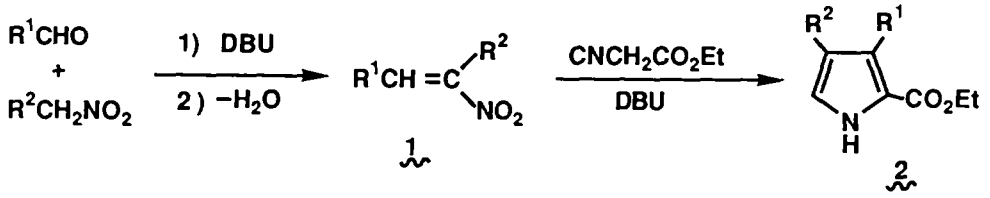
Abstract: A new porphyrin synthesis starting from nitroalkenes or their equivalents is described. For example, octaethylporphyrin, coproporphyrin, porphyrin-1,2,3,4,5,6,7,8 octapropionic acid, and 2,7,12,17 tetraarylporphyrin are prepared in good yield from readily available materials such as 1-nitropropane, nitroethane, nitromethane, and aldehydes.

Nitroalkanes and nitroalkenes are valuable intermediates and their preparative potential in organic synthesis has been well documented.[1] We have been developing new synthetic methods using the nitro function as a leaving group.[2] Such use of the nitro function has opened a new area in organic synthesis. Namely, the nitro group activates many organic reactions such as the aldol condensation, the Michael addition, the Diels-Alder reaction, and radical reactions. Subsequent displacement of the nitro group by hydrogen, carbon, and heteroatoms or elimination of the nitro group to give double bonds provides a very effective strategy for preparing complex organic molecules.[2]

Recently a new synthesis of pyrroles which consists of the reaction of nitroalkenes with isocyanoacetates has been developed.[3] Pyrroles were formed via the Michael addition of isocyanoacetates to nitroalkenes followed by cyclization and elimination of the nitro group. The sequence of these reactions is a typical case where the nitro function plays a dual role: as an activating and as a leaving group. By this method, pyrroles having long alkyl chains[4] or a trifluoromethyl group[5] have been prepared. Compared to the conventional Knorr reaction, this method gave α-free pyrroles directly, and various substituents were readily introduced at the 3 and 4 positions of the pyrrole ring system.



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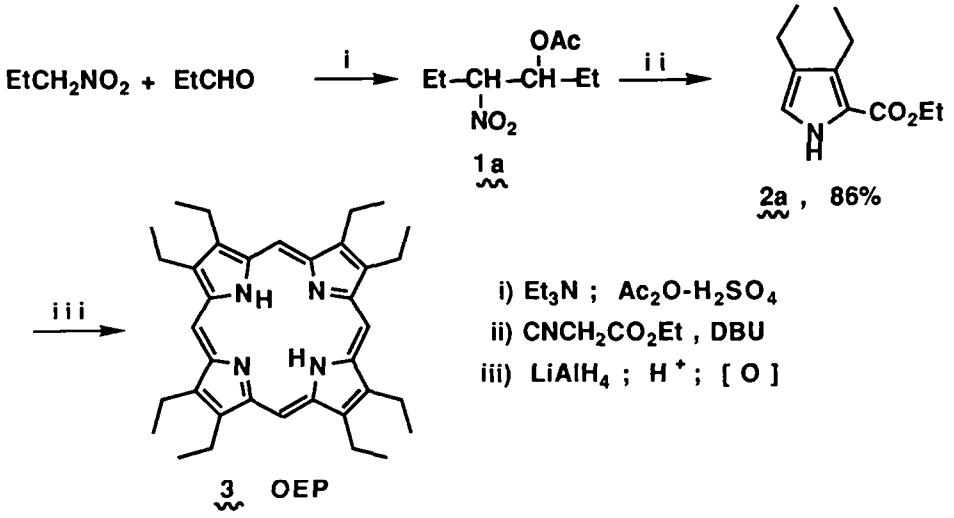
In this paper we wish to report a new synthesis of porphyrins starting from pyrroles (2) which in turn were prepared by the reaction of nitroalkenes (1) or their equivalents with isocyanoacetates (Eq 1). Although conversion of pyrroles prepared by the Knorr reaction has been well established,[6] synthesis of porphyrins from 2 has just started in our laboratory. Our new method gave novel porphyrins which are difficult to prepare by other methods.[5,7]

1. Synthesis of Octaethylporphyrin.

Octaethylporphyrin (OEP) is one of the most important and widely used models for the study of porphyrin chemistry. Therefore, numerous methods to prepare OEP have been devised so far.[8] Most of these start from 2-ethoxycarbonyl-3,4-diethyl-5-methyl pyrrole, which is prepared by the Knorr reaction of ethyl-propionylacetate with 2,4-pentanedione. These methods are inconvenient due to difficulties in preparing starting materials and in transforming the 5-methyl group of the pyrrole ring system. Although the procedures have been extensively modified by many workers,[8] the preparation of OEP is still difficult. A new method, which is summarized in Scheme 1, gave reproducibly high yields in every case. The requisite starting materials were 1-nitropropane, propionaldehyde, and ethyl isocyanoacetate, which are all commercially available.

The key intermediate, ethyl 3,4-diethyl-2-pyrrolecarboxylate (2a), was prepared in 86% yield by the reaction of 3-acetoxy-4-nitrohexane (1a) with ethyl isocyanoacetate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[3] The requisite β-nitro acetate (1a) was prepared in 80% yield by the conventional nitro aldol condensation of 1-nitropropane with propionaldehyde followed by acetylation with acetic anhydride.[9] Conversion of 2a into OEP was carried out in various ways. For example, 2a was converted into OEP via deethoxycarbonylation of the ester function and the Mannich reaction.[8]



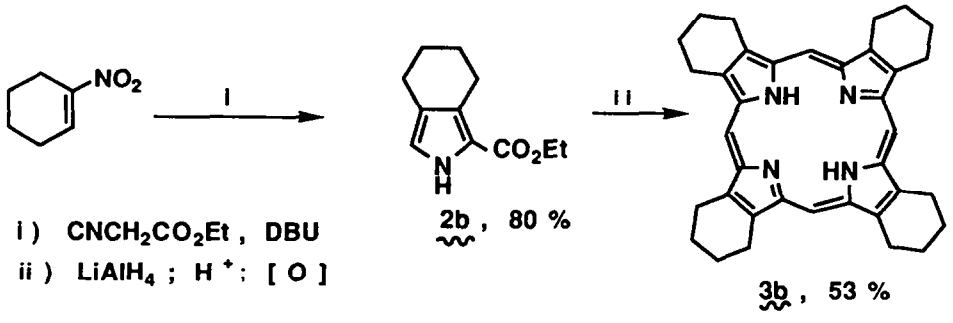
Scheme 1. Preparation of Octaethylporphyrin (OEP).

However, we could not prepare OEP in good yields by this procedure due to the instability of 3,4-diethylpyrrole. We have found a more convenient procedure to convert 2a into OEP. Additionally the procedure is experimentally quite simple. Reduction of 2a with $LiAlH_4$ followed by treatment with an acid and an oxidizing agent gave OEP in 10-55% yields. The yield of OEP depended on the reaction conditions, especially those of the reduction with $LiAlH_4$ and the tetramerization of 2-hydroxymethylpyrrole. The reduction was carried out at low temperature to produce the intermediate 2-hydroxymethylpyrrole in good yield. When the reduction was carried out at higher temperature for a long time, 2-ethoxycarbonylpyrrole was reduced to 2-methylpyrrole with $LiAlH_4$.[10] The conditions of tetramerization of 2-hydroxymethylpyrrole were also important to produce OEP in good yield. The hydroxymethyl group at the α-position of pyrroles was eliminated as formaldehyde by an acid catalyst, additional formaldehyde increased the yield of OEP. Alternatively, methylal was used as an equivalent of formaldehyde. Thus, OEP was prepared by simple procedures and readily available starting materials. The results are summarized in Table

Table 1. Preparation of OEP from 2a.

Reduction of 2a	Cyclization	Oxidation	Yield of OEP, (%)
0 °C 2 h	Ac_2O	O_2	30
25 °C 8 h	Ac_2O	O_2	trace
0 °C 2 h	CH_2Cl_2 , p-TsOH	O_2	23
0 °C 2 h	CH_2Cl_2 , p-TsOH $CH_2(OMe)_2$, (3 equiv)	O_2	52
0 °C 2 h	CH_2Cl_2, p-TsOH $CH_2(OMe)_2$, (3 equiv)	chloranil	55
0 °C 2 h	MeOH , HCOOH $CH_2(OMe)_2$	chloranil	14

The present procedure was extended to the general synthesis of porphyrins which have the same substituents at the β-positions. For example, 1-nitro-cyclohexene was converted to porphyrin 3b in good yield as shown in Eq 2.



i) $CNCH_2CO_2Et$, DBU

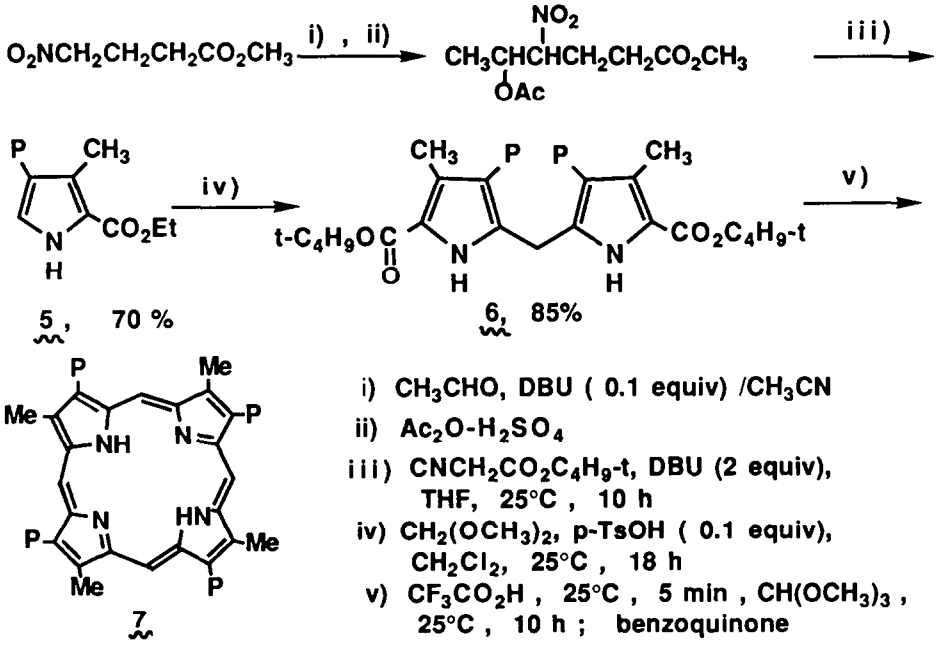
ii) $LiAlH_4$; H^+; [O]

2b, 80 %

3b, 53 %

2. Synthesis of Coproporphyrin and Porphyrin-1,2,3,4,5,6,7,8-octapropionic acid

Porphyrins with propionic acid side chains are found in natural porphyrins. They are not only biologically active but are also useful in the study of porphyrin model systems. For example, such porphyrins have been used for the construction of dimeric, trimeric, and tetrameric porphyrins to study the effect of the enforced aggregation of several metals.[11] Furthermore, porphyrin octaesters exhibit descotic mesophases over a broad temperature range.[12] These porphyrins have been prepared from pyrroles which in turn were prepared by the Knorr reaction between appropriate β-keto esters and β-diketones. However, these methods require tedious lengthy sequences to prepare the desired porphyrins.[13] In this paper we wish to report a simple method to synthesize coproporphyrin (7) and porphyrin-1,2,3,4,5,6,7,8-octapropionic acid octamethyl ester (12). Their preparation is summarized in Scheme 2 and 3, respectively. The common starting material was methyl 4-nitrobutyrate, which was prepared by the Michael reaction of nitromethane with methyl acrylate.



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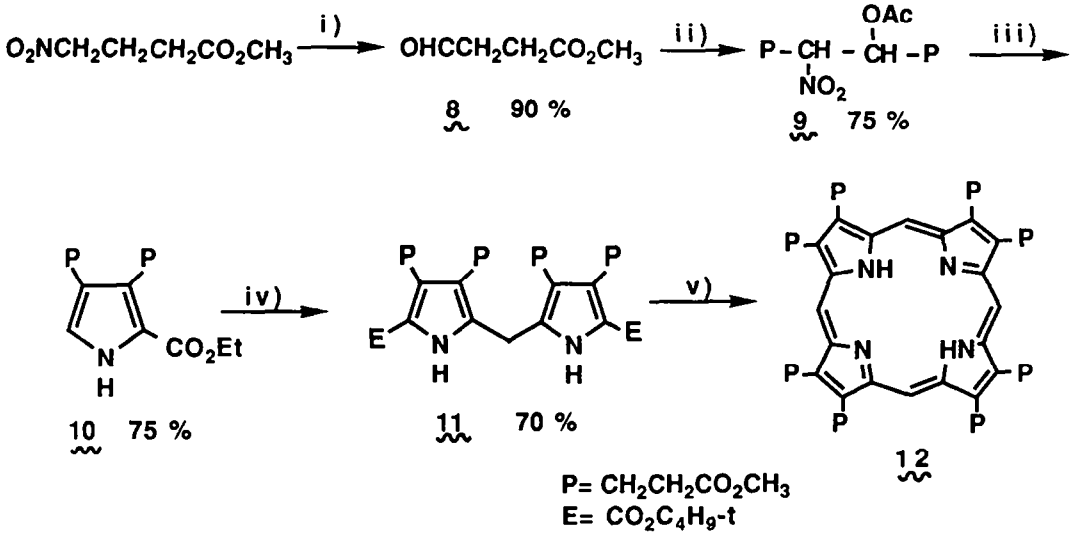
Scheme 2. Synthesis of Coproporphyrin (7).

Nitro aldol condensation of methyl 4-nitrobutyrate with acetaldehyde gave the nitroalcohol, which was converted into the acetate 4 in 70% overall yield. Acetate 4 was treated with t-butyl isocyanoacetate in the presence of DBU to give the α-free pyrrole 5 in 70% yield. Pyrrole 5 was converted into dipyrromethane 6 in 85% yield on treatment with methylal in the presence of p-toluenesulfonic acid (p-TsOH). Finally coproporphyrin 7 was obtained in 25% yield from 6 by reaction with trifluoroacetic acid, followed by treatment with methyl orthoformate. Thus, coproporphyrin 7 was prepared from readily available materials such as nitromethane, methyl acrylate, and acetaldehyde.



i) KOH-MeOH , $KMnO_4$ ii) $O_2NCH_2CH_2CH_2CO_2CH_3$, DBU ; Ac_2O, H_2SO_4
iii) $CNCH_2CO_2C_4H_9$-t , DBU (2 equiv), THF , 25 °C, 10 h .
iv) $CH_2(OCH_3)_2$, p-TsOH (0.1 equiv), CH_2Cl_2 , 25 °C, 18 h .
v) CF_3CO_2H, 25 °C, 5 min ; $CH(OCH_3)_3$, CH_2Cl_2 , 25 °C , 10 h ; benzoquinone .

Scheme 3. Synthesis of Porphyrin-1,2,3,4,5,6,7,8-octapropionic Acid Octamethyl Ester (12).

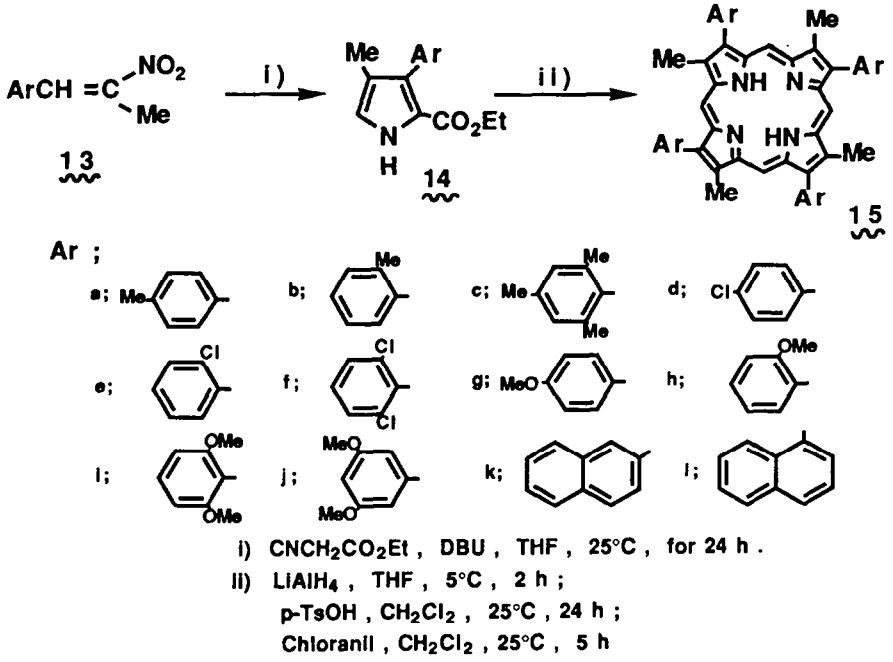
Porphyrin 12, which has eight propionic acid side chains, was also prepared from methyl 4-nitrobutyrate as shown in Scheme 3. The requisite aldehyde 8 was prepared by the Nef reaction of methyl 4-nitrobutyrate.[14] Nitro aldol reaction of 8 with methyl 4-nitrobutyrate followed by acetylation gave 9 in 75% yield. The same procedures as in the synthesis of 7 gave porphyrin 12, The present method for the synthesis of 7 and 12 is far superior to the conventional method which starts from the corresponding pyrroles via the Knorr reactions.[15]

3. Synthesis of 1,3,5,7-Tetraarylporphyrins: New Sterically Hindered Porphyrins.

Recently, sterically hindered tetraaryl porphyrins have become the principal species used not only to model biomimetic transformations, but also to investigate catalytic oxygen transfer and solar energy conversion by synthetic metalloporphyrins.[16] Steric blocking in the porphyrin ring inhibits dimerization and various bimolecular decomposition reactions. Thus, hindered porphyrins are more stable to intramolecular oxidative decomposition than unhindered porphyrins.
Unfortunately, hindered porphyrins are generally obtained in low yields,[17] and furthermore most known hindered porphyrins have bulky aryl groups in the meso (α, β, γ, δ) positions, which causes deviations from planarity of the porphyrin ring. Such porphyrins behave in an unusual manner compared with those that are naturally occurring and the usual model compounds with β-substituents.[6]

In this paper we report the synthesis of a new type of sterically hindered porphyrin with β-aryl substituents which may be more suitable models than meso-tetraarylporphyrins (Scheme 4).

The nitroalkenes (13) were prepared in 60-80% yield by refluxing a mixture of the aldehyde, nitroethane, methylamine hydrochloride, potassium acetate, and methyl orthoformate in MeOH.[18] Such hindered aldehydes as mesitaldehyde and 2,6-dichlorobenzaldehyde gave 13 in good yields by this procedure. The reaction of 13 with ethyl isocyanoacetate gave 14 in 70-80% yield. Here again steric hindrance has no effect on the transformation. The reduction of 14 with $LiAlH_4$ followed by tetramerization with p-TsOH and oxidation with chloranil gave the porphyrins (15) in 50-70% yield. In general, tetramerization of monopyrroles with an acid induces the rearrangement of substituents to give four possible isomers of porphyrins.[19]



i) $CNCH_2CO_2Et$, DBU, THF, 25°C, for 24 h.
ii) $LiAlH_4$, THF, 5°C, 2 h;
p-TsOH, CH_2Cl_2, 25°C, 24 h;
Chloranil, CH_2Cl_2, 25°C, 5 h

Scheme 4. Synthesis of 1,3,5,7-Tetraarylporphyrin (15).

However, we have found that this type of rearrangement is not a serious problem, if the aryl groups are sterically hindered. Namely, type I porphyrins were selectively formed in the preparation of 15b, 15c, 15e, 15f, and 15j. The results are summarized in Table 2, where some spectral data are shown.

The NH chemical shifts are not much affected by the aryl groups, but β-Me and meso-H resonances are shifted to higher field as the aryl groups become large. The UV-Visible absorption maxima are also blue shifted with more bulky aryl groups. The absorption maxima of 15c are very close to those of OEP. These data show that the out-of-plane rotation angles of the aryl groups in 15 change with increasing steric bulk and approach 90° in porphyrin 15c. However, the planarity of the porphyrin ring is maintained in these hindered porphyrins, because the NH resonances all appear in the range δ -3.3 to -3.5.

Table 2. Preparation of 15 and Spectral data of them .

Yield of 15.		NMR δ [a]	λ_{max}/ nm (CH_2Cl_2)	Ms [b]
15a	46%	-3.45 (s, 2H), 2.68 (s,12H), 3.60 (s,12H), 7.66 (d, 8H), 8.06 (d, 8H), 10.15 (s,4H)	418, 506, 540, 572, 626	727
15b	50%	-3.34 (s, 2H), 2.10(m,12H), 3.47 (s,12H), 7.6-8.0 (16H), 9.80 (s, 4H)	410, 501, 536, 568, 622	727
15c	55%	-3.38 (s, 2H), 2.10 (s,12H), 2.17 (s, 24H), 3.24 (s,12H), 7.28 (s, 8H), 9.60 (s, 4H)	403, 499, 531, 565, 620	819
15d	48%	-3.46 (s, 2H), 3.60 (s,2H), 7.5-7.7 (m, 16H), 10.08 (s, 4H)	418, 506, 540, 572, 626	809
15e	50%	-3.38 (s, 2H), 3.41 (s, 12H), 7.5-7.7 (m, 16H), 9.85 (s, 4H)	406, 500, 535, 568, 621	809
15f	70%	-3.35 (s, 2H), 3.37 (s, 12H), 7.6-7.7 (m, 12H), 9.71 (s, 4H)	404, 500, 533, 566, 621	947
15g	56%	-3.41 (s, 2H), 3.67 (s, 12H), 4.09 (s, 12H), 7.75 (m, 16H), 10.12 (s, 4H)	416, 507, 542, 573, 624	791
15h	56%	-3.41 (s, 2H), 3.40 (s, 12H), 4.09 (s, 12H), 7.6 (m, 16H), 9.97 (s, 4H)	409, 505, 540, 573, 624	791
15i	55%	-3.25 (s, 2H), 3.30 (s, 12H), 3.73 (s, 24H), 7.02 (d, 8H), 7.62 (d, 4H), 9.77 (s, 4H)	407, 504, 539, 572, 624	911
15j	50%	-3.44 (s, 2H), 3.62 (s,12H), 4.05 (s,24H), 6.84 (s,4H), 7.32 (s, 8H), 10.22 (s, 4H)	417, 505, 540, 573, 624	911
15k	65%	-3.27, (s, 2H), 3.50 (s, 12H), 7.7-8.8 (m, 28H), 10.23 (s, 4H)	411, 507, 542, 573, 627	863
15l	60%	-3.22 (s, 2H), 3.20 (s, 12H), 7.7-8.5 (m, 28H), 9.55 (s, 4H)	409, 504, 538, 571, 624	863

a) NMR data were recorded in $CDCl_3$ ($5x10^{-3}$ M) at 400 MHz at room temperature with Me_4Si as internal reference.

b) Mass spectra were measured by FAB techniques , where M + 1 peaks appered as parent ions.

Thus, various porphyrins are readily prepared starting from nitro compounds. Compared to conventional methods, the present method has the following merits: (1) α-free pyrroles are prepared in one step; (2) Since nitroalkenes are prepared by a variety of reactions, substituents at the β-position may be changed systematically.

Experimental Section

Ethyl isocyanoacetate and t-butyl isocyanoacetate were prepared by the literature methods.[21] 1-Nitrocyclohexene was prepared by the nitration of cyclohexene. Other materials are commercially available.

Ethyl 3,4-diethylpyrrole-2-carboxylate (2a). A mixture of 3-acetoxy-4-nitrohexane (1a, 16.3 g, 0.083 mol), ethyl isocyanoacetate (9.8 g, 0.087 mol), and DBU (26.4 g, 0.17 mol) in THF (100 ml) was stirred at 20 °C for 12 h. The reaction mixture was poured into water containing 1 M HCl and extracted with ethyl acetate. The extracts were washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (silica gel/CH_2Cl_2-hexane) to give 2a (14.2 g, 86% yield) as oil. IR (neat) 3340, 1680 cm^{-1}. NMR ($CDCl_3$) δ 1.05 -1.42 (9 H, t), 2.40 (2 H, q, J = 7 Hz), 2.60 (2 H, q, J = 7 Hz), 4.24 (2 H, q, J = 7 Hz), 6.70 (1 H, d, J = 3 Hz), 9.28 (1 H, br s). Found: C, 67.42; H, 8.72: N, 7.05%. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Other pyrroles were prepared by this procedure, but when nitroalkenes were used, 1 equivalent of DBU was used.

Octaethylporphyrin (OEP). To a stirred mixture of $LiAlH_4$ (0.32 g, 8 mmol) in dry THF (15 ml) was added a solution of 2a (0.657 g, 3.2 mmol) in THF (5 ml) dropwise at 0-5 °C. The resulting mixture was stirred at 0-5 °C for 2 h. Excess $LiAlH_4$ was destroyed by the addition of ethyl acetate, then the mixture was poured into saturated NH_4Cl solution. The reaction mixture was extracted with ethyl acetate (10 ml x 3). The extract was washed with saturated NaCl solution and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and CH_2Cl_2 (15 ml) was added. To this solution methylal (0.7 ml, 9.6 mmol) and p-TsOH (0.11 g, 0.65 mmol) were added, and the solution was stirred at room temperature for 12 h. Oxidation was carried out either by air or chloranil. The yield of OEP was not affected by the oxidation method. After oxidation, the reaction mixture was washed with aq $NaHCO_3$, and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel/CH_2Cl_2) to give OEP. Recrystallization

from CH_2Cl_2-MeOH gave pure OEP, 0.24 g (55% yield). NMR ($CDCl_3$) δ-3.74 (s, 2 H), 1.93 (t, 24 H), 4.11 (q, 16 H), 10.11 (s, 4 H). $\lambda_{max}(CH_2Cl_2)$ 398, 497, 532, 564, 619 nm. These data were identical with those of an authentic sample.

Porphyrin 3b was prepared by the same procedure as described above: mp 320-325 °C. NMR ($CDCl_3$) δ-3.45 (s, 2 H), 2.56 (br, 16 H), 4.18 (br, 16 H), 10.10 (s, 4 H). λ_{max} (CH_2Cl_2) 398, 499, 535, 566, 619 nm. Fab Mass 527. $C_{36}H_{38}N_4$ requires 526.

Synthesis of Coproporphyrin (7).

t-Butyl 4-(2-methoxycarbonylethyl)-3-methylpyrrole-2-carboxylate (5) was prepared from t-butyl isocyanoacetate and β-nitro acetate (4) by the same method as described in the preparation of 2a. NMR ($CDCl_3$) δ 1.56 (s, 9 H), 1.93 (s, 3 H), 2.5-2.7 (m, 4 H), 3.70 (s, 3 H), 6.72 (d, 1 H, J = 3 Hz), 9.15 (s, 1 H). This pyrrole was converted into dipyrromethane (6) by stirring a mixture of 5 (2.3 g, 10 mmol), methylal (2.0 g, 26.3 mmol), and p-TsOH (0.1 g) in CH_2Cl_2 (50 ml) under N_2 at room temperature for 48 h. After usual work up, the crude product was subjected to column chromatography (silica gel/CH_2Cl_2) to give 6 as a white solid, mp 132-134 °C, Yield 1.7 g (70%). Found: C, 72.22; H, 8.76; N, 5.68. Calcd for $C_{29}H_{42}N_2O_4$: C, 72.17; H, 8.77; N, 5.80. Dipyrromethane 6 (0.48 g, . mmol) was disolved in trifluoroacetic acid (6 ml) and then trifluoroacetic acid was removed under reduced pressure. To this mixture was added CH_2Cl_2 (50 ml) and methyl orthoformate (0.62 g, 6 mmol) under N_2. After 24 h at reflux, the mixture was oxidized by p-benzoquinone (0.11 g, 1 mmol) and reflux continued for 12h. The solution was neutralized by washing with 20% $NaHCO_3$. The organic layer was dried with anhydrous magnesium sulfate and the solvent was removed. The residue was subjected to column chromatography to give porphyrin 7 (0.11 g, 25%), mp 286-289 °C (lit. 286-288 °C).[13] NMR ($CDCl_3$) δ-3.75 (s, 2 H), 3.31 (t, 8 H, J = 7 Hz), 3.675 (OMe, s, 12 H), 3.652 (Me, s, 12 H), 4.45 (t, 8 H, J = 7 Hz), 10.10 (s, 4 H). λ_{max} (CH_2Cl_2) 401, 499, 534, 569, 620 nm.

Synthesis of Porphyrin 1,2,3,4,5,6,7,8-octapropionic acid Octaethyl Ester (12).

Methyl 4-oxobutyrate (8) was prepared in 90% yield by the Nef reaction of methyl 4-nitrobutyrate according to the modified procedure:[21] bp 82 °C/17 mmHg ; NMR ($CDCl_3$) δ 2.3-2.8 (m, 4 H), 3.64 (s, 3 H), 9.75 (s, 1 H). The nitro aldol condensation of this aldehyde with methyl 4-nitrobutyrate was carried out by stirring a mixture of methyl 4-nitrobutyrate (2.54 g, 17.3 mmol), 8 (2.1 g, 18.1 mmol), and DBU (0.1 g) in THF (5 ml). The product was acetylaed with acetic anhydride and H_2SO_4 to

give 9 in 75% yield. NMR ($CDCl_3$) δ1.9-2.6 (m, 8 H), 2.21 (s, 3 H), 3.75 (s, 3 H), 4.82 (m, 1 H), 5.40 (m, 1 H). The pyrrole 10, dipyrromethane 11, and porphyrin 12 were prepared in the same manner as the preparation of 5, 6, and 7, respectively. 10: NMR ($CDCl_3$) δ 1.58 (s, 9 H), 2.53-2.63 (m, 4 H), 2.77 (t, 2 H, J = 7 Hz), 3.00 (t, 2 H, J = 7 Hz), 3.67 (s, 3 H), 3.68 (s, 3 H), 6.67 (d, 1 H, J = 3 Hz), 9.42 (s, 1 H). 11: NMR ($CDCl_3$) δ1.60 (s, 18 H), 2.4-2.63 (m, 8 H), 2.72 (t, 4 H, J = 7 Hz), 3.00 (t, 4 H, J = 7 Hz), 3.65 (s, 3 H), 3.68 (s, 3 H), 6.75 (d, 2 H, J = 8 Hz), 9.42 (s, 2 H). 12: NMR ($CDCl_3$) δ -3.79 (s, 2 H), 3.30 (t, 16 H, J = 8 Hz), 3.64 (s, 24 H), 4.40 (t, 16 H), 10.09 (s, 4 H). λ_{max} (CH_2Cl_2) 406, 502, 537, 573, 627 nm. Fab Mass 999. $C_{52}H_{62}N_4O_{16}$ requires 998. These data were identical with those reported in the literature.[22]

Synthesis of Porphyrin (15i) as a Typical Procedure:

1-(2,6-dimethoxyphenyl)-2-nitropropene (13i). A mixture of nitroethane (3.4 g, 45 mmol), 2,6-dimethoxybenzaldehyde (7.0 g, 42 mmol), CH_3CO_2K (2.4 g, 35 mmol), methylamine hydrochloride (3.4 g, 35 mmol), methyl orthoformate (10 ml), and methanol (30 ml) was stirred at reflux for 7 h. The reaction mixture was poured into water and extracted with ethyl ether. After the usual work up, the crude product was recrystallized from MeOH-Et_2O to give 13i, 7.5 g (80%). mp 102-103 °C. NMR ($CDCl_3$) δ 2.06 (s, 3 H), 3.84 (s, 6 H), 6.48 (d, 2 H, J = 10 Hz), 7.20 (t, 1 H, J = 8 Hz), 7.72 (s, 1 H).

2-Ethoxycarbonyl-3-(2,6-dimethoxyphenyl)-4-methylpyrrole (14i). To a cooled solution of 13i (7.0 g, 31.4 mmol) and ethyl isocyanoacetate (4.5 g, 40 mmol) in THF (60 ml) was added DBU (6.1 g, 40 mmol). The reaction mixture was stirred at 20 °C for 12 h and poured into water. After usual work up, the crude material was recrystallized from EtOH to give 14i, 6.5 g (73%). mp 112-113 °C. NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 8 Hz), 1.76 (s, 3 H), 3.64 (s, 6 H), 4.00 (q, 2 H, J = 8 Hz), 6.44 (d, 2 H, J = 8 Hz), 6.66 (d, 1 H, J = 3 Hz), 7.08 (t, 1 H, J = 8 Hz), 9.36 (s, 1 H). Found: C, 66.29; H, 6.69; N, 4.81. Calcd for $C_{16}H_{19}NO_4$: C, 66.43; H, 6.57; N, 4.84.

Porphyrin (15i). To a stirred mixture of $LiAlH_4$ (0.32 g, 8 mmol) in dry THF (30 ml) was added a solution of 14i (0.89 g, 3.1 mmol) in THF (5 ml) dropwise at 0-5 °C. The resulting mixture was stirred at 0-5 °C for 2 h. After the same treatment as described in the preparation of OEP, the crude product was purified by column chromatography (silica gel/CH_2Cl_2) to give 15i, 0.36 g (50%). The spectral data are summarized in Table 2. Other porphyrins were prepared in the same way as the preparation of 15i.

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