92, 2313 (1970).
(9) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, 723 (1969).
(10) S. D. Morse, K. A. Laurence, G. H. Sprenger, and J. M. Shreeve, *J. Fluorine Chem.*, 11, 327 (1978).
(11) D. E. Young and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **7**, 1033 (1971).
(12) D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Commun.*, 736 (1971).
(13) A. Haas and U. Niemann, *Adv. Inorg. Chem. Radiochem.*, **18**, 143 (1976).
(14) (a) H. W. Roesky and S. Tutkunkardes, *Chem. Ber.*, **107**, 508 (1974); (b) D. T. Sauer and J. M. Shreeve, *Inorg. Chem.*, **10**, 358 (1971); (c) D. T. Sauer and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **6**, 501 (1970); (d) C. A. Burton and J. M. Shreeve, *Inorg. Chem.*, **16**, 1039 (1977).
(15) T. Kitazume and J. M. Shreeve, *J. Fluorine Chem.*, **9**, 175 (1977); *J. Am. Chem. Soc.*, **99**, 3690 (1977).
(16) (a) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2339 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997 (1972); (c) C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969); (d) R. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); (e) G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972).
(17) (a) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974); (b) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 549 (1969); (c) O. Ruff, *Chem. Ber.*, 4513 (1904); (d) I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952).
(18) T. M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 5634 (1975); J. C. Martin and T. M. Balthazor, *ibid.*, **99**, 152 (1977).
(19) A. Majid and J. M. Shreeve, *Inorg. Chem.*, **13**, 1710 (1974).
(20) C. T. Ratcliffe and J. M. Shreeve, *J. Am. Chem. Soc.*, **90**, 5403 (1968).
(21) Q. C. Mir, D. P. Babb, and J. M. Shreeve, *J. Am. Chem. Soc.*, **101**, 3961 (1979).
(22) W. Gombler, *Angew. Chem., Int. Ed. Engl.*, **16**, 723 (1977).
(23) T. Kitazume and J. M. Shreeve, *J. Am. Chem. Soc.*, **100**, 492 (1978).
(24) W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1971).
(25) W. A. Sheppard and S. S. Foster, *J. Fluorine Chem.*, **2**, 53 (1972).
(26) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).
(27) J. I. Darragh and D. W. A. Sharp, *Angew. Chem., Int. Ed. Engl.*, **9**, 73 (1970).
(28) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2341 (1971).
(29) L. J. Kaplan and J. C. Martin, *J. Am. Chem. Soc.*, **95**, 793 (1973).
(30) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **93**, 6674 (1971).
(31) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **94**, 5010 (1972).
(32) D. Schomburg, private communication.
(33) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

Novel Meso-Substitution Reactions of Metalloporphyrins

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Abstract: Solutions of octaalkyl metalloporphyrin π cation radicals react with nucleophiles such as nitrite, chloride, pyridines, imidazole, cyanide, triphenylphosphine, thiocyanate, acetate, and azide, to produce the corresponding meso- (methine) substituted metalloporphyrins. Demetalation then gives the appropriate meso-substituted porphyrin. Circumstantial evidence suggests that the π cation radical reacts (possibly in a complexed or aggregated form) with the nucleophile, and that the corresponding π dication of the metalloporphyrin or the radical (produced by oxidation of the nucleophile) is not involved in the combination step of the reaction.

Introduction

The classical methods for introduction of substituents into the meso (methine) positions of porphyrins involve electrophilic substitution upon the porphyrin nucleus.[2] However, since the classical deuteration, nitration, halogenation, sulfonation, formylation, and acetylation procedures require use of acidic reagents, and because the N,N′-diprotonated porphyrin salt is nonnucleophilic, it is necessary to protect the inner porphyrin nitrogens against protonation in situ by formation of a metal complex. Nickel(II), copper(II), and iron(III) complexes are most often used, but these suffer two disadvantages in that they (1) are relatively difficult to demetalate after the reaction and (2) are relatively electron withdrawing, thereby causing a decrease of electron density in the porphyrin ligand which is being employed as a nucleophile. Both of these disadvantages are assessed relative to zinc(II), cadmium(II), or magnesium(II) complexes which are easy to demetalate in high yield and which "release" electron density to the porphyrin ligand; unfortunately, use of these more favorable metal complexes for classical electrophilic meso substitution in porphyrins causes almost instantaneous demetalation (even in the relatively mild Vilsmeier formylation procedure employing phosphoryl chloride and dimethylformamide).

The prospect of using alternative methods[3] for meso substitution was brought to our attention by a report which showed that aromatics (e.g., perylene) can be nitrated using nitrite and the corresponding aromatic π cation radical.[4] It transpires that there now exists an extensive literature on the reactions of such π cation radicals with a whole variety of nucleophiles, and the mechanistic pathway of these transformations has many times been demonstrated to involve reactions of the π cation radical rather than, for example, the π dication.[5] Our interest was yet further stimulated by the fact that metalloporphyrin π cation radicals can be readily formed, either chemically or electrochemically; moreover, though metalloporphyrin π cation radicals had been shown to be stable in methanol,[6] a relatively good nucleophile, the corresponding π dications are extremely potent electrophiles,[7] so we considered that at the least we could use these two-electron oxidation products as substrates. We were hopeful, however, that, if the metalloporphyrin π cation radicals were found to be as reactive as other aromatic π cation radicals, then it would be possible to prepare the porphyrin analogues in methanol and to dissolve the nucleophiles in the same solvent without the danger of obtaining meso methoxy-substituted products.

Results and Discussion

Nitration. Treatment of magnesium(II) etioporphyrin I (**1**) in chloroform with an excess of iodine (i.e., 4 oxidizing equiv) in methanol gave a green solution of the π cation radical possessing a characteristic electronic absorption spectrum.[6] Addition of sodium nitrite (as a suspension in methanol) caused a rapid color change to give a red solution, the visible spectrum of which, though of the normal metalloporphyrin type, suggested that a chemical transformation of the porphyrin ligand had occurred. Demetalation and chromatography gave a small amount of etioporphyrin I (**2**) and an 84% yield of the corresponding meso mononitro derivative **3**. A similar procedure

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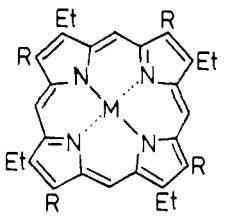
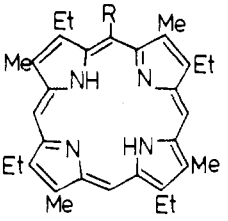


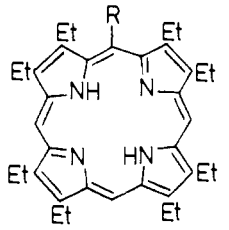
1 M = Mg, R = Me
4 M = Mg, R = Et
6 M = Zn, R = Et
20 M = Mg, PY_2, R = Et
27 M = Ni, R = Et
31 M = Cu, R = Et



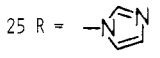
2 R = H
3 R = NO_2
34 R = OAc
35 R = N_3
36 R = NH_2

using magnesium(II) octaethylporphyrin (**4**) gave a 79% yield of **5**.

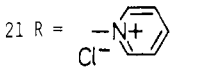
Zinc(II) complexes of porphyrins are more conveniently prepared than are magnesium(II) complexes;[8] thus, preparation of *meso*-nitrooctaethylporphyrin from zinc(II) octaethylporphyrin (**6**) would be advantageous but iodine is not a strong enough oxidant to abstract an electron from zinc complexes.[6] Treatment of zinc(II) octaethylporphyrin (**6**) with tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate[9] $[(C_6H_4Br)_3N^+ \cdot SbCl_6^-]$ generated the π cation radical, and addition of a solution of sodium nitrite in methanol caused a rapid change in color from green to red. After an acidic workup an excellent yield of *meso*-nitrooctaethylporphyrin (**5**) was obtained. When zinc(II) octaethylporphyrin (**6**) was treated with 1-chlorobenzotriazole[10] the π cation radical was again generated. Addition of sodium nitrite followed by demetalation

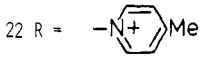


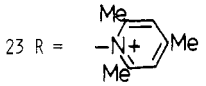
5 R = NO_2
14 R = H
18 R = Cl

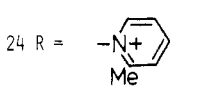


26 R = CN
28 R = PH_3P^+ Cl^-
32 R = SH
33 R = SCN
37 R = OMe



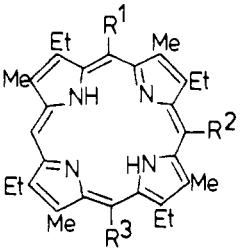


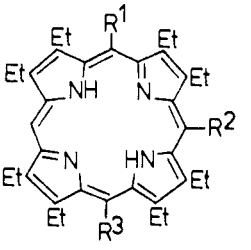




gave a 66% yield of *meso*-nitrooctaethylporphyrin (**5**). Cadmium(II) porphyrins have an oxidation potential lower than that of zinc(II) and similar to those of magnesium(II) porphyrins.[11] Moreover, cadmium(II) porphyrins are more easily prepared than the magnesium analogues. Treatment of magnesium(II) etioporphyrin I π cation radical (generated using iodine as above) with a solution of silver nitrite in acetonitrile, followed by immediate demetalation and chromatography, gave crystalline porphyrinic material in almost quantitative yield. Its composition was shown by NMR spectroscopy to be substantially the meso mononitroporphyrin **3** with about 5% of unreacted etioporphyrin I (**2**). If either the zinc(II) or magnesium(II) etioporphyrin chelates was treated with 1 equiv of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate, a solution of the π cation radical was again formed. This reacted readily with silver nitrite added in acetonitrile and the crystalline material **3**, isolated as above, was characterized by NMR and mass spectroscopy. On the basis of the anticipated stoichiometry for a two-electron oxidation, this procedure should yield an equimolar mixture of etioporphyrin I (**2**) and its monosubstituted derivative **3**. In practice, recovery of the unsubstituted porphyrin was invariably much lower than anticipated, with the α-nitro compound **3** accounting for most of the product mixture; furthermore, yields often exceeded the theoretical maximum.

In addition to these findings it was noted that, on standing, the silver nitrite–porphyrin solutions became green, and spectrophotometry indicated further transformation of the organic material. The mass spectrum of material isolated after prolonged reaction times showed peaks consistent with substitution of nitrite ion for one, two, three, and four meso protons. It became evident that the silver nitrite, present in large excesses, was also oxidizing the ligand, in the latter case allowing further nitration to give dinitroporphyrins and ultimately tetrasubstituted products by replacement of all four meso protons. Also, the low recovery of etioporphyrin (**2**) (from the reactions involving ammoniumyl salt above) was seen to depend upon the presence of silver ion whose reduction [Ag(I) + e → Ag(0)] accomplished removal of the second electron. Thus, in contrast to the iodine reactions, those involving silver nitrite led to further substitution, reflecting the higher oxidizing strength of the latter system. For example, on stirring a solution of magnesium(II) etioporphyrin I (**1**) with silver nitrite in chloroform–methanol–acetonitrile solution for about 18 h at room temperature, a mixture of di- (**7, 8**) and tri- (**9**)





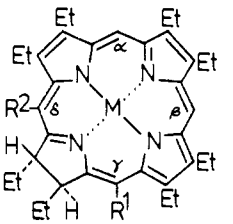
7 R^1 = R^2 = NO_2, R^3 = H
8 R^1 = R^3 = NO_2, R^2 = H
9 R^1 = R^2 = R^3 = NO_2

10 R^1 = R^2 = NO_2, R^3 = H
11 R^1 = R^3 = NO_2, R^2 = H
19 R^1 = R^3 = Cl, R^2 = H

nitroetioporphyrins was formed. Chromatographic separation allowed isolation of the dinitro derivative in 79% yield. A similar procedure using the octaethylporphyrin chelate again gave dinitroporphyrins (**10** and **11**) as the major products, along with a small amount of the mononitroporphyrin **5**. The isomers were separated according to the method of Bonnett et al.[12] or by thin layer or silica gel column chromatography. From the experimental results, and known oxidation potential data,[11] it follows that (1) values of $E^1_{1/2}$ for α-nitroporphyrin magnesium chelates most probably lie in the range of $0.55 < E^1_{1/2} < 0.8$ V, i.e., between the E^0 values for iodine (0.55 V) and silver(I) (0.8 V), and (2) formation of small amounts of the trisubstituted etioporphyrin suggests that $E^1_{1/2}$ for the dinitro derivative is around 0.8 V. Absence of trinitroporphyrin from the magnesium(II) octaethylporphyrin reaction suggests that its dinitroporphyrin precursor has a value of $E^1_{1/2} > 0.8$ V. This minor distinction in properties between the two porphyrins is also explicable in terms of oxidation potentials, assuming that the difference existing in the unsubstituted chelates [magnesium(II) octaethylporphyrin = 0.54 V, magnesium(II) etioporphyrin I = 0.40 V][13] also exists in the cor-

responding nitroporphyrins. The oxidation potentials of the metal-free meso nitrooctaethylporphyrins have been measured by Johnson and Dolphin[14] (octaethylporphyrin, 0.86 V; mononitro, 1.1 V; dinitro, 1.3 V; trinitro, 1.46 V; tetranitro, >1.6 V).

The meso-nitration reaction was extended to include dihydroporphyrin systems. On mixing solutions of zinc(II) *trans*-octaethylchlorin (**12**) and 2 oxidizing equiv of iodine, the blue-green color of the metallochlorin gave way to a brown solution of its π cation radical. The oxidized species persisted in the presence of methanol, but on addition of sodium nitrite a grass-green solution was obtained. The mixture was treated with acid to afford metal-free material, and visible absorption spectra and TLC indicated the presence of porphyrinic material and at least two chlorin components. Large-scale separation led to the isolation of mononitrochlorin **13** which was always found to be the major product in these reactions. Other products isolated included octaethylporphyrin (**14**), α-nitrooctaethylporphyrin (**5**), *trans*-octaethylchlorin (**15**), and the γ,δ-dinitrochlorin **16**. This route represents an efficient



12 M = Zn, $R^1 = R^2 = H$
13 M = 2H, $R^1 = NO_2$, $R^2 = H$
15 M = 2H, $R^1 = R^2 = H$
16 M = 2H, $R^1 = R^2 = NO_2$
17 M = Zn, $R^1 = NO_2$, $R^2 = H$

route to γ-nitrochlorin **13**, the octaethylchlorin derivative being formed in 65% yield. The small quantities of porphyrin isolated are probably artifacts of the oxidative reaction since dehydrogenation of the chlorin or its π cation radical may also occur in the presence of iodine. Formation of significant amounts of the dinitrochlorin **16** from reactions involving zinc(II) octaethylchlorin (**12**) and 1 molecular equiv of iodine indicates that, in addition to the starting material, its γ-nitro derivative is also oxidized, and at a comparable rate under these conditions. This further process consumes iodine required in the second oxidation step. Unreacted zinc(II) octaethylchlorin π cation radical could serve this function and account for the recovery of starting material (as octaethylchlorin). Iodine oxidation of zinc(II) γ-nitrooctaethylchlorin (**17**) was verified in a reaction involving it and an excess of iodine, to yield a brown π cation radical solution which could be converted into quantities of the γ,δ-dinitro derivative **16** by addition of sodium nitrite followed by an acidic workup. It was hoped that the latter reaction, or one employing zinc(II) octaethylchlorin and an excess of iodine, might provide an efficient synthesis of the disubstituted chlorin **16**. Unfortunately, mixtures of mono- and disubstituted compounds were invariably obtained and separation, either as their zinc complexes or after demetalation, was incomplete. The use of ferric perchlorate as oxidant in place of iodine was no more successful in this respect; even 4 oxidizing equiv of the ferric salt, though effective in generating the brown π cation radical, did not give a clean conversion to the dinitrochlorin **16**.

Chlorination. Oxidation of magnesium(II) octaethylporphyrin (**4**) with iodine rapidly gave a solution of the π cation radical, and upon addition of tetraethylammonium chloride in methanol the color of the solution quickly changed from green to red. However, after an acidic workup, a quantitative recovery of octaethylporphyrin (**14**) was obtained. Thus, in this case, the anion appears to be reducing the π cation radical rather than undergoing nucleophilic attack upon it. When zinc(II) octaethylporphyrin (**6**) was oxidized to its π cation radical using tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate and treated with tetraethylammonium chloride, the color of the solution slowly turned red when a fivefold excess was added over a period of time. After an acidic workup, three porphyrinic compounds were present and these could be separated using preparative TLC. The most polar compound was identified as octaethylporphyrin (**14**) and the material isolated in greatest yield (31%) was shown to be *meso*-chlorooctaethylporphyrin (**18**). Only minor quantities of the third compound were present and from mass spectral data it was clearly a *meso*-dichlorooctaethylporphyrin. When the reaction was repeated without addition of tetraethylammonium chloride, the color of the cation radical solution gradually turned red; after an acidic workup the dichloroporphyrin was the only characterizable product. The NMR spectrum of the compound clearly indicated that only one dichloro isomer was present and that this had the α,γ orientation of substituents, as in **19**. It is not immediately obvious how the chloroporphyrins are obtained in these circumstances but it is tempting to suggest that there is some free chloride in the hexachloroantimonate and this reacts with the cation radical. The hexachloroantimonate of tris(*p*-bromophenyl)amine cation radical is more stable than the perchlorate and this large counterion appears to be a prerequisite for metalloporphyrin π cation radicals to react with chloride as a nucleophile; its role could be to stabilize the π cation radical against reduction. The reduction of aromatic cation radicals by chloride appears to be a general phenomenon and Shine[15] found that treatment of the π cation radical of perylene with chloride gave only perylene and free halogen.

Reaction of octaethylporphyrin with hydrogen peroxide in the presence of hydrochloric acid has been shown[16] to give a mixture of *meso*-chlorooctaethylporphyrin (**18**) and α,γ-dichlorooctaethylporphyrin (**19**) (as the sole disubstituted product). It is interesting to consider whether there is a mechanistic link between the π cation radical reaction with chloride and the hydrogen peroxide reaction as the same dichloroporphyrins are obtained. Hydrogen peroxide should be able to oxidize octaethylporphyrin (**14**) to its π cation radical which could then react with chloride from hydrochloric acid, although there is no recent experimental evidence to substantiate this suggestion.

Pyridination. There are many examples of aromatic hydrocarbons (when oxidized anodically or with iodine) reacting with pyridine. Oxidation of benzo[*a*]pyrene with iodine in the presence of pyridine has been shown[17] to give the *N*-(6-benzo[*a*]pyrenyl)pyridinium ion. Anodic oxidation of 9,10-diphenylanthracene in the presence of pyridine led to a dipyridinium ion and the reaction has been interpreted[18] as involving direct attack of the pyridine upon the π cation radical. We had earlier found that, when dipyridinemagnesium(II) octaethylporphyrin (**20**) was treated with thallium(III) nitrate followed by addition of pyridine, a polar product was observed during the chromatographic workup, and this was shown to be the meso-pyridinium porphyrin salt **21**, though the nature of the counterion at that time could not be established by elemental analysis. The meso-pyridinium derivative of etioporphyrin I was also obtained by oxidizing the magnesium(II) complex to the π cation radical followed by reaction with pyridine. It was found spectrophotometrically that decay of the π cation radical absorption was slow with pyridine alone; however, the rate of reaction increased dramatically in the presence of ferric perchlorate. The suggestion that pyridine reacted directly with solutions of the π cation radical to generate the porphyrin has been substantiated by Shine et al.,[19] who observed that the π cation radical from zinc(II) *meso*-tetraphenylporphyrin, as its perchlorate salt, reacted with

pyridine to give the corresponding β-substituted pyridinium salt.

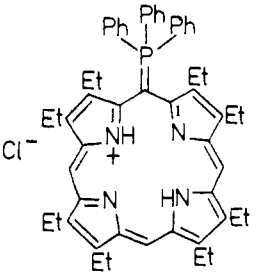
meso-Pyridinium octaethylporphyrin (**21**) was found to be more conveniently synthesized by treating zinc(II) octaethylporphyrin (**6**) with thallium(III) nitrate followed by addition of pyridine. Demetalation, using hydrochloric acid, and washing of the compound with aqueous sodium chloride enabled it to be analyzed as the hydrated chloride salt (isolated in 45% yield). During the chromatographic purification a forerun was eluted and this was shown to be *meso*-nitrooctaethylporphyrin (**5**), obtained by direct reaction[20] of the thallium(III) nitrate. Use of 4-methylpyridine in place of pyridine in the reaction gave the *meso*-4-methylpyridinium porphyrin **22** in 32% yield. Similarly 2,4,6-trimethylpyridine gave the porphyrin **23** in low yield (8%), whereas use of 2-methylpyridine gave very little *meso*-2-methylpyridinium porphyrin **24.** Use of pyrimidine gave no meso-substituted product and this may be explained by the low pK_a of pyrimidine (1.23).[21] The low yield in the reaction with collidine may also be explained by steric effects due to the 2- and 6-methyl functions of the collidine. It is likely that the lower pK_a of 2-methylpyridine (5.91)[22] compared with that of collidine (7.43)[21] reduces the nucleophilicity of the compound to such an extent that it cannot overcome the steric repulsion in the transition state.

Reaction with Imidazole. Metalloporphyrins have been incorporated into a polymeric matrix of polystyrene containing 20% of 1-vinylimidazole as copolymer through the coupling of a meso carbon to an imidazole nitrogen.[23] Oxidation of magnesium(II) octaethylporphyrin (**4**) with benzoyl peroxide generated the π cation radical and this subsequently coupled with the polymer. Treatment of zinc(II) octaethylporphyrin π cation radical [obtained using thallium(III) nitrate] with imidazole in chloroform gives a 7% yield of the polar meso imidazole derivative **25.** Large quantities of octaethylporphyrin (90%) and a little *meso*-nitrooctaethylporphyrin (2%) were also recovered from this reaction.

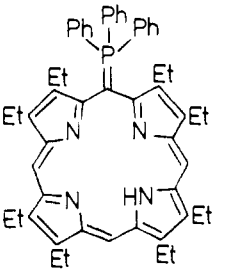
Cyanation. Aromatic nitriles are produced during the anodic oxidation of aromatic compounds in solutions containing cyanide ion. The oxidation potential of cyanide ion is quite low (0.96 V) and Koyama[24] interpreted the anodic oxidation of anisole in the presence of sodium cyanide, which gives a mixture of *o*- and *p*-cyanoanisoles, as involving attack by the electrochemically generated cyano radical as a strong electron acceptor on the points of high electron density in the aromatic compounds. However, Nilsson[25] has shown, from controlled-potential experiments and isomer distribution determinations (coupled with the fact that cyanide ion has a high overpotential on platinum due to the formation of cyanide compounds as a film on the electrode surface), that this mechanism could be ruled out. It was considered that anodic cyanation could be best described as a nucleophilic attack by cyanide ion on a π cation radical formed by an initial one-electron transfer from the substrate to the anode. Shine has shown[26] that perylene π cation radical reacts with potassium cyanide to give a mixture of 1- and 3-cyanoperylene, the reaction being interpreted as involving direct attack of the cyanide anion upon the π cation radical.

In synthetic metalloporphyrin chemistry there are very few examples of the formation of meso-carbon to carbon substituent bonds; namely, these are formylation,[27] methylation,[28] and nitromethylation.[29] *meso*-Cyanooctaethylporphyrin (**26**) is obtained by a long synthetic sequence involving formylation of the nickel(II) complex **27,** demetalation, oxime formation, and finally dehydration. Any method which would accomplish the preparation of the meso cyanoporphyrin directly from a metal complex of octaethylporphyrin would thus be very useful synthetically. Treatment of a solution of zinc(II) octaethylporphyrin (**6**) with tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate generated a green solution of the π cation radical which upon addition of a methanolic solution of sodium cyanide gradually turned red. After demetalation using hydrochloric acid, the porphyrinic material was separated from tris(*p*-bromophenyl)amine using column chromatography. The compound, which gave a very characteristic visible absorption spectrum, was identified as *meso*-cyanooctaethylporphyrin (**26**). A 68% yield was obtained, and thus this method for the preparation of the compound is synthetically advantageous. During the course of the reaction no *meso*-methoxyporphyrin was detected. The *meso*-cyanoporphyrin was also obtained when zinc(II) octaethylporphyrin (**6**) was treated with 1-chlorobenzotriazole and sodium cyanide, although this procedure has synthetic limitations because the product has to be separated from some unchanged octaethylporphyrin (**14**).

Reaction with Triphenylphosphine. Over the last 25 years, the Wittig reaction for the synthesis of olefins[30] has assumed great importance in synthetic organic chemistry[31] and it seemed that introduction of a *meso*-triphenylphosphonium substituent onto the porphyrin nucleus would extend the reaction to these systems. Treatment of zinc(II) octaethylporphyrin (**6**) with tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate gave the π cation radical, and this was treated with triphenylphosphine. The zinc was removed from the products using hydrochloric acid and thin layer chromatography indicated the presence of a polar, green compound which was purified by column chromatography. The NMR spectrum of the green compound indicated meso substitution and the complex resonances between δ 7.90 and 6.50 showed that a triphenylphosphonium substituent was present. Decomposition of the compound to give octaethylporphyrin and triphenylphosphine occurred in the mass spectrometer. Analytical data identified the product, obtained in 26% yield, as the phosphonium salt **28** but the visible absorption spectrum indicated that there was a significant resonance contribution from the porphyrin cation **29.** Unfortunately, in preliminary experiments,



29



30

the phosphonium salt was shown to be stable in the presence of sodium methoxide and *n*-butyraldehyde, limiting at the moment the extension of the Wittig reaction into porphyrin chemistry. This could be due to the highly stabilized ylide **30** and steric repulsion of the reactants. Structure **30** possesses a variant of the theoretically interesting isoporphyrin chromophore.[7] Shine[19] has reported that tetraphenylporphyrin π cation radical reacts with triphenylphosphine but full details of this generically different product have not been reported.

Thiocyanation. Meso thiocyanatoporphyrins have been encountered as intermediates in the synthesis of meso thiolporphyrins.[32] Treatment of copper(II) octaethylporphyrin (**31**) with thiocyanogen gave the corresponding *meso*-thiocyanatoporphyrin which was hydrolyzed to give the thiol **32** using 90% sulfuric acid. It seemed that the thiocyanatoporphyrin should be accessible from thiocyanate reacting with a solution of π cation radical. Zinc(II) octaethylporphyrin (**6**) was oxidized to its π cation radical by reaction with the ammoniumyl salt and a solution of sodium thiocyanate in methanol was added slowly. After an acidic workup a mixture of products resulted and these were separated, using thick layer chroma-

tography. The minor products were *meso*-chlorooctaethylporphyrin (**18**) and octaethylporphyrin (**14**), but the major product (53% yield) was the expected *meso*-thiocyanatoporphyrin **33**. Bonnett[33] has recently reported the successful formation of similar compounds by reaction of porphyrin π cation radicals with thiocyanate and other nucleophiles.

Acetoxylation. Evidence for meso acetoxylation of metalloporphyrin π cation radicals was obtained in experiments using magnesium(II) etioporphyrin I (**1**), iodine, and tetraethylammonium acetate. From these, a mixture of mono- and diacetoxyporphyrins was generally formed, together with unreacted starting material **2**. Separation of the constituents by preparative TLC using silica met with moderate success, though it gave quantities of pure material inadequate for total analysis. Identification was based largely upon mass spectrometry, which showed peaks at *m/e* 536 and 594 consistent with mono- and diacetoxylation, respectively. Spectrophotometry suggested meso substitution in both cases and characterization of the monoacetoxy compound **34** was aided by comparison with authentic material prepared by a different route involving oxophlorins.[34]

Trifluoroacetoxylation. An efficient route to *meso*-trifluoroacetoxyporphyrins[34] and -chlorins[35] using magnesium(II) or zinc(II) porphyrins or chlorins and thallium(III) trifluoroacetate as the oxidant has already been described.

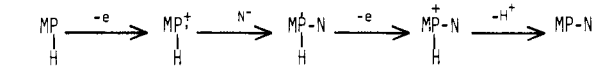
Other Nucleophiles. During the course of these studies several other nucleophiles (N) were employed in attempts to generate meso-substituted products, both from zinc(II) and magnesium(II) porphyrins. These attempts proved unsuccessful for cases in which N = F^-, Br^-, I^-, CH_3^-, $C_2H_5^-$, and CH_3O^-, owing to reduction of the π cation radical. In the case N = N_3^-, spectrophotometry provided evidence for a clean reaction to give a meso azidoporphyrin **35** which was never able to survive the workup procedure. Hydrogenation of the product mixture in tetrahydrofuran over 10% palladized charcoal, followed by chromatography, gave etioporphyrin I (**2**) as the only recognizable product. Isolation of *meso*-aminoporphyrin **36** (also prepared using a reductive route[36] from the corresponding nitroporphyrin **3**) would have provided strong chemical evidence for a meso-azido complex formed with the π cation radical solution.

From a consideration of the above examples, one may conclude that the efficiency of these reactions is not directly related to the nucleophilic strength of the attacking species.

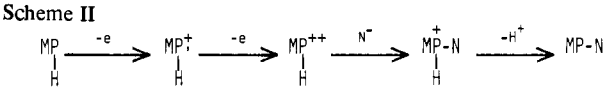
Mechanistic Considerations. Though the above discussion refers repeatedly to reactions of solutions of metalloporphyrin π cation radicals with nucleophiles, there is little direct or hard evidence to confirm that it is indeed the π cation radical itself which reacts with the nucleophile. Neither, at the present time, is it known which electronic state ($^2A_{1u}$ or $^2A_{2u}$)[37] of the spectrophotometrically observed cation radical is involved with subsequent transformations. What is certain, however, is that the π cation radical of the metalloporphyrin is produced, in solution, on the pathway toward meso-substituted porphyrin.

There are nominally three major pathways, each involving cation radical ($M(H)P^{+\cdot}$), which could be proposed for the transformations outlined above and these are given in Schemes I-III. In Scheme I the metalloporphyrin (MP-H) is transformed into its π cation radical ($M(H)P^{+\cdot}$) which suffers attack by nucleophile (N^-) to give a radical. Subsequent loss of an electron and a proton gives the required meso-substituted metalloporphyrin (MP-N). This basic mechanism is the one firmly established for many reactions of aromatic π cation radicals with nucleophiles.[5] Scheme II shows two consecutive one-electron abstractions from the metalloporphyrin to give the π dication ($M(H)P^{2+}$) before attack by nucleophile and loss of a proton to give MP-N. This type of mechanism has been shown to be operative under circumstances where the π dication ($M(H)P^{2+}$) is obtained.[7] Finally, Scheme III shows combination of a radical (obtained by oxidation of the nucleophile) with a π cation radical, followed by loss of a proton. This process has been implicated in the reaction of nitrogen dioxide with metalloporphyrin π cation radicals.[14]

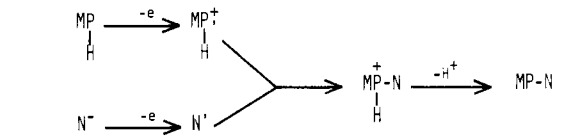
Scheme I



Scheme II



Scheme III



We can qualitatively eliminate Scheme II because most of our reactions have been run in methanol as solvent. Methanol reacts very rapidly with the π dication ($M(H)P^{2+}$) to give *meso*-methoxyporphyrin[7] but the π cation radical is stable in methanol.[6] At no time did we observe formation of *meso*-methoxyporphyrin **37** so we can conclude that the π dication was not an intermediate in the transformation.

Scheme III is less easy to dismiss. Such a π cation radical and radical combination was suggested[38] in an early procedure for synthesis of pheoporphyrins, though this was subsequently challenged[7] in favor of a mechanism of the type in Scheme II (even though the solvent was methanol). For the particular case of meso trifluoroacetoxylation,[34b] one might expect[39] that the trifluoroacetoxy radical (N·) might decarboxylate at such a rate that *meso*-trifluoromethylporphyrin would be observed. None was. To clarify the situation with regard to Scheme III, we have carried out the reactions in the presence of urea as a NO_2 trap. The I_2/NO_2^- reaction was repeated in the presence of urea and after an acidic workup an identical quantity of *meso*-nitrooctaethylporphyrin (**5**) was isolated as from a blank containing no urea. However, when the nitrogen dioxide reaction[14] was carried out in the presence of urea, a greatly reduced yield of *meso*-nitrooctaethylporphyrin was isolated compared to the yield in the absence of urea. From this we conclude that nitrogen dioxide is not formed from nitrite in the former reaction.

Perhaps the most convincing evidence against oxidation of the nucleophile is provided by the fact that the oxidation of pyridine to give the corresponding radical (for the pyridination reaction) requires greater than 2.0 V (in CH_3CN at Pt vs. SCE),[5] far in excess of the potential accessible using iodine as the oxidant. Moreover, Nilsson's work[25] on the anodic cyanation reaction has also eliminated oxidation of cyanide as a viable process in that case.

While there is no strong reason to suggest that all of the metalloporphyrin π cation radical reactions follow the same mechanistic pathway, it seems reasonable to suggest that this is so until more kinetic evidence on porphyrin systems is available. At the present time it seems sound to propose that the mechanism roughly follows that outlined in Scheme I. It is, however, possible that complexation (with a large counterion, such as hexachloroantimonate) or aggregation of the π cation radical ($M(H)P^{+\cdot}$) occurs before its reaction with nucleophile. This has been shown to take place in other nonporphyrin studies,[40] and it is a fact that zinc(II) porphyrins[41] and metalloporphyrin π cation radicals[42] do aggregate strongly. Moreover, recent work by Dolphin et al.[43] suggests that aggregation of the cation radical may be important in the specific reaction of it with pyridine. The effect of aggregation or complexation on the electronic state of the porphyrin is,

nevertheless, not understood at this time; neither is it known whether one or other of the electronic ground states of the π cation radicals[37] are required for successful reactions.

Experimental Section

Melting points were measured on a microscopic hot stage apparatus. TLC monitoring of all reactions was performed using Merck silica gel 60 F-254 precoated sheets (0.2 mm), and preparative TLC was carried out on 20 × 20 cm glass plates coated with Merck GF 254 silica gel (1.5 mm). Column chromatography was carried out on Merck neutral alumina 90 (70–230 mesh). Electronic absorption spectra were determined using a Cary 15 spectrophotometer (solutions in CH_2Cl_2), and ^1H NMR spectra were measured, usually in $CDCl_3$ solution with tetramethylsilane as internal standard, at 100 MHz (Varian XL-100 or JEOL PFT-100). Mass spectra (direct insertion probe, 70 eV, 50 μA, source temperature ~200 °C) were measured using an AE1 MS9 instrument.

The zinc(II) and cadmium(II) porphyrin substrates used in these studies were prepared according to standard literature procedures employing the appropriate metal acetate salt.[8] The magnesium chelates were prepared[8] as their dipyridinates; axial pyridine ligands could be efficiently removed using the procedure of Fuhrhop and Mauzerall.[44] Etioporphyrin I was synthesized from pyrromethenes.[45] *trans*-Octaethylchlorin was prepared following the procedure of Whitlock et al.[46] from the iron(III) porphyrin.

Meso Nitration. A. Using $NaNO_2$. *meso*-Nitroetioporphyrin I (3). (a) From Magnesium(II) Etioporphyrin I (1). A solution of 25 mg of the ligand-free metal complex in 30 mL of chloroform was treated with 26.7 mg of iodine in 5 mL of chloroform and 5 mL of acetonitrile to generate the green solution of the metalloporphyrin π cation radical. A solution of 138 mg of sodium nitrite in 30 mL of methanol was then added, producing an immediate color change to red. Trifluoroacetic acid was added directly to the solution, which was left for about 2 min, then washed with water, dried (Na_2SO_4), and evaporated to dryness. Chromatography on alumina (grade II, elution with benzene) and crystallization from dichloromethane–methanol gave the meso nitroporphyrin (22 mg, 84%). A small quantity of etioporphyrin I (**2**) was also eluted from the column. The product was characterized by NMR, visible, and TLC comparison with an authentic sample prepared using a standard procedure.[12,47]

(b) From Cadmium(II) Etioporphyrin I. Low solubility of the cadmium(II) porphyrin substrate necessitated a slight modification to the above procedure. A solution of 26.7 mg of iodine in 30 mL of chloroform and 20 mL of methanol was used and the mixture was stirred for 30 min at room temperature to give a solution of the π cation radical. On treatment with 138 mg of sodium nitrite in 15 mL of methanol the green solution turned orange-red in color. Acidic workup and chromatography as above gave the meso nitroporphyrin **4** (18 mg, 69%). Continued elution of the column gave etioporphyrin I (estimated 2 mg).

***meso*-Nitrooctaethylporphyrin (5)** was prepared from magnesium(II) octaethylporphyrin (**4**) following procedure (a) above. Chromatographic separation of the demetalated product mixture was achieved on alumina (Grade II) using a carbon tetrachloride–dichloromethane solvent system. Elution with CCl_4–10% CH_2Cl_2 gave a small quantity of the dinitro derivatives **7** and **8.** The major meso-nitroporphyrin fraction was eluted in carbon tetrachloride–15% dichloromethane and this was followed by octaethylporphyrin (estimated 4 mg). The main band was crystallized from dichloromethane–methanol to give red-brown rhombs (21 mg, 79%), mp 241–243 °C (lit.[12] 239–240 °C). NMR, visible, and TLC data were identical with those of an authentic sample.[12]

γ-Nitrooctaethylchlorin (13). A solution of 60 mg of zinc(II) octaethylchlorin dissolved in 20 mL of chloroform was treated with a solution of 28 mg of iodine in 5 mL of dry methanol to give a brown solution of the metallochlorin π cation radical. On addition of a solution of 0.5 g of sodium nitrite in 25 mL of dry methanol the solution turned grass-green in color; after 5 min this was washed with water and the organic product was extracted with dichloromethane. The organic solvents were removed and the resulting solid was redissolved in a minimum volume of dichloromethane and treated with trifluoroacetic acid to demetalate. After neutralization (H_2O) and drying (Na_2SO_4) the solution was evaporated to dryness. Chromatography on alumina (grade II) eluting with carbon tetrachloride gave the following fractions: (a) γ,δ-dinitrooctaethylchlorin (**16**), crystallized from dichloromethane–*n*-hexane (4 mg), mp 241–242 °C (lit.[12] 242.5–243 °C); (b) γ-nitrooctaethylchlorin (**13**); (c) *trans*-octaethylchlorin (**15**); (d) *meso*-nitrooctaethylporphyrin (**5**); (e) octaethylporphyrin (**14**). Undemetalated porphyrin and chlorin complexes remained on top of the column. The major fraction [band (b)] was crystallized from dichloromethane–*n*-hexane to give the γ-nitrochlorin **13** (31 mg, 53%), mp 206–211 °C (lit.[12] 218–219 °C). Anal. Calcd for $C_{36}H_{47}N_5O_2$: C, 74.32; H, 8.14; N, 12.04. Found: C, 74.30; H, 8.22; N, 11.95. NMR: δ 9.83, 9.57, 8.82 (3 meso H), 4.70 (1 H, broad d, β-H), 4.42 (1 H, broad s, β-H), 4.1–3.4 (12 H, m, 6 CH_2CH_3), 1.9–1.5 (24 H, m, 8 CH_2CH_3), 0.93 (4 H, q, 2 CH_2CH_3).

In another reaction [using zinc(II) octaethylchlorin and 3 equiv of I_2] the products were separated prior to demetalation. Use of deactivated (grade V) alumina and elution with carbon tetrachloride–dichloromethane (4:1) gave the zinc(II) chelate, **17.** Demetalation (TFA) and crystallization (dichloromethane–*n*-hexane) gave the γ-nitrochlorin **13** in 65% yield (25-mg scale), mp 215–218 °C (lit.[12] 218–219 °C).

The zinc complex, **17,** re-formed in chloroform–methanol solution was crystallized from dichloromethane–*n*-hexane, mp 199–202 °C. Anal. Calcd for $C_{36}H_{45}N_5O_2Zn$: C, 67.02; H, 7.03; N, 10.86. Found: C, 67.28; H, 7.14; N, 10.58. Visible λ_{max} ($CHCl_3$) 398 nm (ε 76 600), 505 (4500), 588 (6300), and 625 (35 200). MS: *m/e* 643 (100%), 321.5 (8).

γ,δ-Dinitrooctaethylchlorin (16). A solution of 15 mg of zinc(II) γ-nitrooctaethylchlorin (**17**) in 5 ml of chloroform was treated with a solution of 16 mg of iodine in 5 mL of methanol. The solution turned green-brown in color indicating partial formation of the π cation radical species; on addition of a further 16 mg of iodine the solution darkened. Addition of 200 mg of sodium nitrite in 5 mL of methanol regenerated the green chlorin color. The product mixture was evaporated to dryness and the organic solid was taken up in carbon tetrachloride. Chromatography on alumina (grade V) gave three main bands. Elution with carbon tetrachloride–dichloromethane (9:1) gave porphyrinic material; using carbon tetrachloride–dichloromethane (1:1) a small quantity of the zinc(II) γ-nitrochlorin **17** was eluted and in neat dichloromethane a second green fraction was obtained. Demetalation (TFA) and neutralization (H_2O) gave the γ,δ-dinitrochlorin **16,** which was crystallized from dichloromethane–*n*-hexane (7 mg, 48%), mp 238–241 °C (lit.[12] 242.5–243 °C). The γ-nitro- and γ,δ-dinitrochlorins from these reactions could be distinguished by visible absorption spectroscopy.[12]

B. Using $AgNO_2$. *meso*-Nitroetioporphyrin I (3). (a) From Dipyridinemagnesium(II) Etioporphyrin I. A solution of 50 mg of the magnesium(II) porphyrin in 50 mL of dichloromethane was treated with a solution of 21 mg of iodine in 10 mL of acetonitrile and 40 mL of dichloromethane. The mixture was treated with 100 mg of silver nitrite in 10 mL of acetonitrile and the red metalloporphyrin solution so formed was immediately washed with water (to remove the excess of silver nitrite); the organic liquors were dried (Na_2SO_4) and evaporated to dryness before demetalation (TFA) and neutralization (several washings with H_2O). The product was chromatographed on a short alumina column (grade V), the red-brown eluates being collected and the product crystallized from dichloromethane–methanol to give a lustrous, purple solid (39 mg, 98%). The visible absorption spectrum was consistent with an α-nitroporphyrin structure, though its NMR spectrum showed ca. 5% of etioporphyrin I impurity, not separated in the chromatographic step.

(b) From Zinc(II) Etioporphyrin I. A solution of 114 mg of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in 10 mL of acetonitrile and 20 mL of dichloromethane was added to a solution of 100 mg of the zinc(II) porphyrin in 30 mL of dichloromethane and 10 mL of tetrahydrofuran to give a purple π cation radical solution. This was treated with 200 mg of silver nitrite in 20 mL of acetonitrile; immediate aqueous workup of the red solution was followed by demetalation as above. The solid product mixture was taken up in the minimum volume of dichloromethane and chromatographed on alumina (grade II). Elution with benzene gave two bands: (a) α-nitroetioporphyrin I (**3**) and (b) etioporphyrin I (**2**). Band (a) was crystallized (CH_2Cl_2–MeOH) to give a crop of purple crystals identical by TLC, NMR, and spectrophotometry with an authentic sample.[12,46] Anal. Calcd for $C_{32}H_{35}N_5O_2$: C, 73.39; H, 7.29; N, 13.37. Found: C, 73.28; H, 7.29; N, 13.10. MS: *m/e* 523 (100%).

Meso Dinitroporphyrins. From Magnesium(II) Etioporphyrin I (1). A solution of 10 mg of the ligand-free magnesium complex in 15 mL

of chloroform was treated with 350 mg of silver nitrite in 10 mL of acetonitrile and 15 mL of dry methanol. The resulting suspension was stirred overnight at room temperature to yield an orange-red metalloporphyrin solution. Addition of chloroform to precipitate the silver nitrite and filtration were followed by aqueous washing (to remove any remaining silver salt). The organic phase was dried (Na_2SO_4) and evaporated to dryness; demetalation using trifluoroacetic acid (1 mL) gave an emerald-green solution which was neutralized prior to chromatography (grade II alumina, elution with benzene) to give the meso dinitroporphyrin [α,β (**7**) and α,γ (**8**) isomers] as major products crystallized from dichloromethane–methanol (9 mg, 79%). The isomeric mixture was identified by its visible absorption spectrum; separation could be achieved by fractional crystallization using the method of Bonnett and Stephenson.[12]

Meso Chlorination. *meso*-Chloroetioporphyrin I. A solution of 100 mg of zinc(II) etioporphyrin I in refluxing chloroform–tetrahydrofuran (60 mL, 5:1) was treated with 310 mg of tris(*p*-bromophenyl)-ammoniumyl hexachloroantimonate in dichloromethane–acetonitrile (50 mL, 4:1) to generate the π cation radical species. Addition of a solution of 37 mg of tetraethylammonium chloride monohydrate in dichloromethane–acetonitrile (20 mL, 1:3) to the green solution at ca. 50 °C effected a color change to purple. This color changed little on standing (viz., its electronic absorption spectrum) so a further 170 mg of tetraethylammoniumyl chloride in 15 mL of acetonitrile was added and the flask was swirled to form a red metalloporphyrin solution which was found (spectrophotometry) to be free of π cation radical. The product was washed twice with water, dried (Na_2SO_4), and evaporated to dryness. Demetalation in refluxing trifluoroacetic acid–chloroform–methanol (1:1:1) was followed by neutralization (aqueous $NaHCO_3$ and water) and the organic solution was dried (Na_2SO_4) and evaporated to dryness. Analytical TLC [on silica, using chloroform–benzene (3:1) as eluting solvent] and spectrophotometry indicated the formation of *meso*-monochloroporphyrin in <50% yield. This was purified by dissolving in the minimum of dichloromethane and addition of an equal volume of benzene. Evaporation of the dichloromethane gave a solution of the porphyrin material in hot benzene which was poured onto an alumina column (grade II). Elution with benzene yielded three fractions: (a) dichloroetioporphyrin I (minor quantity), (b) *meso*-chloroetioporphyrin I, and (c) etioporphyrin I (**2**). Material from band (b), crystallized from CH_2Cl_2–*n*-hexane, had mp >300 °C. Anal. Calcd for $C_{32}H_{37}ClN_4$: C, 74.90; H, 7.27; N, 10.92. Found: C, 74.03; H, 7.22; N, 10.65. MS: *m/e* 512 (100%), 256 (15). NMR: δ 10.04 (2 H, s, 2 meso H), 9.84 (1 H, meso H), 4.3–3.8 (8 H, m, CH_2CH_3), 3.64, 3.56, 3.54, 3.48 (4 CH_3), 1.81 (6 H, t, 2 CH_2CH_3), 1.78 (6 H, t, 2 CH_2CH_3).

***meso*-Chlorooctaethylporphyrin (18).** A solution of 902 mg of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in 100 mL of dichloromethane was added to a stirred solution of 300 mg of zinc(II) octaethylporphyrin in 30 mL of THF and 100 mL of CH_2Cl_2. To the green solution, 375 mg of tetraethylammonium chloride in 50 mL of CH_2Cl_2 was slowly added and the mixture was stirred for 2 h. A solution of 5 mL of hydrochloric acid in 10 mL of THF was added and after stirring for 5 min the mixture was poured into 300 mL of water. The CH_2Cl_2 phase was washed with 300 mL of water, dried (Na_2SO_4), and evaporated. Chromatography of the resulting solid on silica plates using light petroleum–toluene (60:40) as eluant gave three bands. Extraction of the middle band into $CHCl_3$–methanol gave a red solution from which upon concentration of the solvents the product crystallized as purple prisms (99 mg, 31%): mp 270–272 °C (lit.[16] 270–272 °C); MS *m/e* 570 (45%), 568 (100), and 534 (16); NMR δ 10.08 (2 H, s, 2 meso H), 9.84 (1 H, s, meso H), 4.30–3.95 (16 H, m, $-CH_2CH_3$), and 2.00–1.77 (24 H, m, $-CH_2CH_3$).

Meso Pyridination. *meso*-(*N*-Pyridinium)octaethylporphyrin Chloride (21). A solution of 300 mg of zinc(II) octaethylporphyrin in 30 mL of THF was flushed with nitrogen for 10 min prior to the addition of a solution of 234 mg of thallium(III) nitrate in 25 mL of dry methanol. After stirring for 30 s, 10 mL of pyridine was added; after stirring for 30 min, SO_2 gas was bubbled into the solution. Hydrochloric acid (20 mL) was added to the residue obtained on evaporation of the solvents and after stirring for 5 min the mixture was poured into 300 mL of $CHCl_3$, washed with 300 mL of brine, dried ($CaCl_2$), and evaporated. The solid obtained was chromatographed on alumina (grade V) using $CHCl_3$ as eluant and a red forerun containing mainly octaethylporphyrin (**14**, 74 mg) was obtained. Further elution of the column with $CHCl_3$–5% methanol gave red eluates which were washed with brine, dried ($CaCl_2$), and evaporated. Crystallization of the residue from CH_2Cl_2–*n*-hexane gave the product as purple, fluffy needles (147 mg, 45%; 60% yield based on consumed octaethylporphyrin), mp >300 °C. Anal. Calcd for $C_{41}H_{50}ClN_5 \cdot H_2O$: C, 73.90; H, 7.86; Cl, 5.32; N, 10.51. Found: C, 74.03; H, 7.85; Cl, 5.24; N, 10.62. Visible: λ_{max} 402 nm (ϵ 150 100), 505 (14 400), 537 (11 500), 566 (8500), and 616 (8300). MS: *m/e* 611 (15%) and 534 (100). NMR: δ 10.21 (2 H, s, meso H), 9.90 (1, s, meso H), 9.50–9.20 (3 H, m, meta and paraaromatic H), 8.80–8.50 (2 H, m, orthoaromatic H), 4.10–3.60 (12 H, m, $-CH_2CH_3$), 2.30–2.00 (4 H, m, $-CH_2CH_3$), 2.00–1.50 (18 H, m, $-CH_2CH_3$), and 1.30–0.80 (6 H, m, $-CH_2CH_3$).

Meso Substitution with Collidine (2,4,6-Trimethylpyridine). To a solution of 50 mg of zinc(II) octaethylporphyrin was added a solution of 75 mg of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in dichloromethane–acetonitrile (50 mL, 4:1). To the blue solution 0.3 mL of collidine was added and the solution turned purple in color, visible absorption spectroscopy showing the presence of π cation radical (ca. 650 nm). A further 0.3 mL of collidine was added and the solution was left for 15 min; a visible spectrum indicated meso substitution to have occurred. Demetalation of the product solution (TFA) and neutralization (two aqueous washings) gave a product with a "phyllo"-type electronic absorption spectrum. Chromatography in dichloromethane gave two mobile bands: (a) a red component identified as octaethylporphyrin (**14**) and (b) an unidentified brown fraction. Continued elution in dichloromethane–5% methanol yielded a second brown fraction which was crystallized from dichloromethane–*n*-hexane to give the product **23:** mp >300 °C; NMR δ 10.19 (2 H, s, 2 meso H), 10.00 (1 H, s, meso H), 9.20 (2 H, s), 4.20–3.80 (12 H, m, 6 CH_2CH_3), 2.93 (3 H, s, CH_3), 2.50–2.20 (4 H, m, 2 CH_2CH_3), 2.10–1.60 (18 H, m, 6 CH_2CH_3), 1.29 (6 H, t, 2 CH_2CH_3).

Reaction with Imidazole. Synthesis of 25. A mixture of 76 mg of zinc(II) octaethylporphyrin and 470 mg of imidazole in 20 mL of dry $CHCl_3$ under nitrogen was treated with 60 mg of thallium(III) nitrate dissolved in 5 mL of dry methanol. The solution was stirred at room temperature for 16 h before SO_2 gas was bubbled through the mixture for 30 s, followed by addition of 1 mL of hydrochloric acid in 5 mL of THF. The solution was diluted with $CHCl_3$ and washed with water, saturated sodium bicarbonate solution, then water again. Evaporation and reevaporation of toluene gave a residue which was chromatographed on silica thick layer plates, eluting with 2% methanol in CH_2Cl_2. The product, **25,** was isolated as a slow-running purple zone and was crystallized from CH_2Cl_2–*n*-hexane (5.6 mg, 7.3%), mp 214–215 °C. Anal. Calcd for $C_{39}H_{48}N_6$. C, 77.96; H, 8.05; N, 13.99. Found: C, 78.30; H, 8.24; N, 13.71. Visible: λ_{max} 400 nm (ϵ 151 500), 500 (13 300), 535 (8700), 569 (6300), and 622 (4700). MS: *m/e* 600 (100%), 533 (20), NMR: δ 10.24 (2 H, s, meso H), 10.05 (1 H, s, meso H), 8.47, 7.90, 7.60 (each 1 H, s, 3 imidazole H), 4.10 (12 H, m, CH_2CH_3), 2.66 (4 H, m, CH_2CH_3), 1.90 (18 H, m, CH_2CH_3), 1.58 (6 H, m, CH_2CH_3). Also isolated were 61 mg of octaethylporphyrin (**14**) and 3 mg of *meso*-nitrooctaethylporphyrin (**5**).

Meso Cyanation. *meso*-Cyanooctaethylporphyrin (26). (a) From *meso*-Formyloctaethylporphyrin. A mixture of 780 mg of *meso*-formyloctaethylporphyrin and 1.25 g of hydroxylamine hydrochloride in 300 mL of pyridine was heated on a steam bath for 1.25 h. The mixture was poured into 1 L of water and the precipitated solid was filtered onto Celite. The Celite was washed with $CHCl_3$ and the filtrate evaporated giving a red solid which was chromatographed on alumina (grade V) with CH_2Cl_2 as eluant. A dark purple band containing 205 mg of starting material was first eluted and this was followed by a red band; the eluates were evaporated and the solid obtained was crystallized from CH_2Cl_2–light petroleum as a bright red fluff (572 mg, 71%; 97% yield based on consumed starting material) to give the oxime, mp 252–254 °C (lit.[27] 249–250 °C). Anal. Calcd for $C_{37}H_{47}N_5O$: C, 76.91; H, 8.20; N, 12.12. Found: C, 77.13; H. 8.11; N, 11.84. Visible: λ 402 nm (ϵ 153 200), 502.5 (14 100), 535.5 (9100), 570 (6000), and 623 (4200). MS: *m/e* 577 (6%) and 559 (100). NMR: δ 10.60 (1 H, s, CH=NOH), 10.15 (2 H, s, 2 meso H), 10.00 (1 H, s, meso H), 7.45 (1 H, s, CH=NOH), 4.20–3.80 (16 H, m, $-CH_2CH_3$), and 2.00–1.70 (24 H, m, $-CH_2CH_3$). A solution of the foregoing oxime of *meso*-formyloctaethylporphyrin in 250 mL of acetic anhydride was heated under reflux for 1 h. Water (500 mL) was added, the mixture was stirred for a further 1 h before being extracted into 300 mL of $CHCl_3$, and the extract was washed with 500 mL of water, dried (Na_2SO_4), and evaporated. Chromatography of the solid obtained on alumina using CH_2Cl_2 as eluant gave a purple

band which was collected and the eluates were evaporated. Crystallization of the resulting solid from CH_2Cl_2–light petroleum gave purple microneedles (420 mg, 67%) of the required *meso*-cyanoporphyrin **26**, mp 254–255 °C (lit.[27] 260 °C). Anal. Calcd for $C_{37}H_{45}N_5$: C, 79.39; H, 8.10; N, 12.51. Found: C, 79.34; H, 8.00; N, 12.59. Visible: λ_{max} 404 nm (ϵ 123 700), 511.5 (10 400), 548 (13 400), 579 (6200), and 631.5 (12 800). IR (KBr): 2200 cm^{-1} (CN). MS: *m/e* 559 (100%) and 534 (48). NMR: δ 10.08 (2 H, s, 2 meso H), 9.98 (1 H, s, meso H), 4.40–3.90 (16 H, m, $-CH_2CH_3$), and 2.05–1.75 (24 H, m, $-CH_2CH_3$).

(b) Direct from Zinc(II) Octaethylporphyrin (6). A solution of 28 mg of 1-chlorobenzotriazole in 25 mL of $CHCl_3$ was added to a solution of 100 mg of zinc(II) octaethylporphyrin (**6**) in 100 mL of $CHCl_3$ stirred under an atmosphere of nitrogen. The color of the solution immediately turned green and a solution of 100 mg of sodium cyanide in 25 mL of methanol was slowly added. After 5 min, 2 mL of hydrochloric acid in 10 mL of methanol was added to the red solution, and after stirring for 5 min the mixture was poured into 200 mL of water. The $CHCl_3$ phase was washed with 200 mL of water, dried (Na_2SO_4), and evaporated. Chromatography on alumina of the resulting solid using CH_2Cl_2 as eluant gave a red forerun containing some octaethylporphyrin (**14**) and this was followed by deep purple eluates which were evaporated. The solid obtained was crystallized from CH_2Cl_2–methanol as purple microneedles (52 mg, 56%), the material obtained being identical with that described in (a).

(c) To a stirred mixture of 300 mg of zinc(II) octaethylporphyrin in 20 mL of THF containing 100 mL of CH_2Cl_2 and 120 mg of sodium cyanide in 20 mL of methanol was added to a solution of 902 mg of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in 100 mL of CH_2Cl_2. After 2 h the solution was washed with 250 mL of 15% hydrochloric acid and 2 × 50 mL of water, dried (Na_2SO_4), and evaporated. The solid obtained was column chromatographed on silica gel using toluene as eluant; a forerun containing tris(*p*-bromophenyl)amine was discarded. Elution of the column with CH_2Cl_2 gave deep purple eluates which were evaporated and the solid was crystallized from CH_2Cl_2–methanol as purple, fluffy needles (204 mg, 68%). The material obtained was identical with that described above.

***meso*-Cyanoetioporphyrin I.** This compound was prepared using a cyanide method similar to that described above for *meso*-cyanooctaethylporphyrin (**26**). It was obtained in 70% yield and crystallized from $CHCl_3$–methanol as purple needles, mp >300 °C. Anal. Calcd for $C_{33}H_{37}N_5$: C, 78.69; H, 7.40; N, 13.90. Found: C, 78.56; H, 7.52; N, 13.75. Visible: λ_{max} 402 nm (ϵ 148 400), 510.5 (9900), 547 (12 700), 580 (5600), and 633 (11 500). IR: 2200 cm^{-1} (CN). MS: *m/e* 503 (100%) and 478 (43). NMR: δ 10.06 (2 H, s, 2 meso H), 9.99 (1 H, s, meso H), 4.30–3.85 (8 H, m, $-CH_2CH_3$), 3.72, 3.62, 3.57, 3.55 (each 3 H, s, 4 CH_3), and 2.00–1.70 (12 H, m, $-CH_2CH_3$).

***meso*-Triphenylphosphonium Octaethylporphyrin Chloride (28).** A solution of 1.2 g of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in 250 mL of CH_2Cl_2 was added to a stirred solution of 400 mg of zinc(II) octaethylporphyrin (**6**) in 100 mL of CH_2Cl_2 and 50 mL of THF. After stirring for 1 min, a solution of 263 mg of triphenylphosphine in 50 mL of CH_2Cl_2 was added and the mixture was stirred for 15 min. The mixture was washed with 500 mL of 15% hydrochloric acid and 2 × 500 mL of water, then dried (Na_2SO_4) and evaporated. Chromatography of the solid obtained on alumina (grade V) using CH_2Cl_2 as eluant gave a red band which was discarded. Further elution of the column with CH_2Cl_2–5% methanol gave bright green eluates which were evaporated and the residue was crystallized from CH_2Cl_2–diethyl ether–*n*-hexane as dark green prisms (147 mg, 26%), mp >300 °C. Anal. Calcd for $C_{54}H_{60}ClN_4P$: C, 78.00; H, 7.27; N, 6.74. Found: C, 77.69; H, 7.27; N, 6.89. Visible: λ_{max} 421 nm (ϵ 117 200), 608 (8200), and 677 nm (16 500). MS: *m/e* 534 (100%) and 262 (65). NMR: δ 9.79 (1 H, s, meso H), 9.62 (2 H, s, 2 meso H), 7.85–6.55 (15 H, m, phenyl H), 4.25–2.65 (16 H, m, $-CH_2CH_3$), 2.00–1.80 (12 H, m, $-CH_2CH_3$), 1.46 (6 H, t, $-CH_2CH_3$), and 1.24 (6 H, t, $-CH_2CH_3$).

***meso*-Thiocyanatooctaethylporphyrin (33).** A solution of 600 mg of tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in 100 mL of CH_2Cl_2 was added to a stirred mixture of 200 mg of zinc(II) octaethylporphyrin (**6**) and 150 mg of sodium thiocyanate in 100 mL of CH_2Cl_2, 30 mL of THF, and 25 mL of methanol. After stirring for 2 h the mixture was washed with 250 mL of 15% hydrochloric acid and 2 × 250 mL of water and then dried (Na_2SO_4). The solid obtained on evaporation of the extracts was chromatographed on silica plates using toluene as eluent and the most polar, dark purple band was extracted into $CHCl_3$. Evaporation of the solvent and crystallization of the residue from CH_2Cl_2–methanol gave purple prisms (104 mg, 53%), mp >300 °C. Anal. Calcd for $C_{37}H_{45}N_5S$: C, 75.09; H, 7.66; N, 11.83. Found: C, 74.87; H, 7.65; N, 11.82. Visible: λ_{max} 405 nm (ϵ 122 400), 511.5 (8500), 548 (9400), 580 (4500), and 631 (6900). IR (KBr): 2140 cm^{-1} (CN). MS: *m/e* 591 (34%) and 534 (100). NMR: δ 10.11 (2 H, s, 2 meso H), 9.95 (1 H, s, meso H), 4.60–3.92 (16 H, m, $-CH_2CH_3$), and 1.96–1.78 (24 H, m, $-CH_2CH_3$).

Meso Acetoxylation. A solution of 25 mg of magnesium(II) etioporphyrin I (**1**) in 20 mL of chloroform was treated with a solution of 32 mg of iodine in 5 mL of $CHCl_3$. Addition of 250 mg of tetraethylammonium acetate tetrahydrate caused an immediate color change to red. The product was then subjected to the usual procedure of demetalation (TFA), neutralization (H_2O), and evaporation to dryness. Passage of a dichloromethane solution of the metal-free material down a short alumina column (grade II) gave a red porphyrinic band followed by a green band of oxophlorin material (spectrophotometry). Analytical TLC of the red fraction [on silica using *n*-hexane–acetone (70:30)] indicated three porphyrinic components. Using the same system, separations on a preparative scale were attempted. The major (red-brown) fraction (having intermediate R_f value) was crystallized from dichloromethane–methanol. Mass spectroscopy showed it to be a mixture of etioporphyrin I and its *meso*-acetoxy derivative. MS: *m/e* 536 (43%) [M^+], 494 (100) [$M^+ - COCH_2$], 478 (100), M* 455 (536 → 494). The most polar band (pink-red), also crystallized from dichloromethane–methanol, was found to be a mixture (mass spectrum). *meso*-Diacetoxyporphyrin could be identified: MS *m/e* 594 (12%) [M^+], 552 (12) [$M^+ - COCH_2$], 510 (4) [$M^+ - 2COCH_2$], 536 (3), 494 (24), 478 (100), M* 513 (594 → 552), and 471 (552 → 510).

Meso Substitution Using Sodium Azide. A solution of 25 mg of magnesium(II) etioporphyrin I (**1**) in 25 mL of chloroform was treated with a solution of 26.7 mg of iodine in 10 mL of chloroform, 3 mL of acetonitrile, and 5 mL of methanol to form the green π cation radical solution. Sodium azide (32 mg) in 10 mL of methanol was then added and the solution turned red-brown in color immediately. The visible absorption spectrum of the product indicated that meso substitution had taken place, presumably to form the *meso*-azidoetioporphyrin I magnesium complex. All attempts to isolate this compound, or the metal-free porphyrin from this reaction, resulted in decomposition to unidentified materials.

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References and Notes

(1) (a) University of California at Davis. (b) University of Liverpool.
(2) Fuhrhop, J.-H. In "Porphyrins and Metalloporphyrins", Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 645–659.
(3) Part of this work has been the subject of preliminary publications: Barnett, G. H.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1974**, 772–773. Barnett, G. H.; Evans, B.; Smith, K. M., *Tetrahedron Lett.* **1976**, 4009–4012. Evans, B.; Smith, K. M., *Ibid.* **1977**, 3079–3082.
(4) Ristagno, C. V.; Shine, H. J. *J. Am. Chem. Soc.* **1971**, *93*, 1811–1812.
(5) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155–278. Eberson, L.; Nyberg, K. *Ibid.* **1976**, *12*, 1–129. *Tetrahedron* **1976**, *32*, 2185–2206. Evans, J. F.; Lenhard, J. R.; Blount H. N. *J. Org. Chem.* **1977**, *42*, 983–988, and references cited therein.
(6) Dolphin, D.; Muljiani, A.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 177–198.
(7) Dolphin, D.; Felton, R. H.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1970**, *92*, 743–745.
(8) Reference 2, pp 796, 798.
(9) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719–2720.
(10) Storr, R. C.; Rees, C. W. *J. Chem. Soc. C* **1969**, 1474–1477. Smith, J. R. L.; Sadd, J. S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 741–747.
(11) Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140–5147. See also ref 2, pp. 593–666.
(12) Bonnett, R.; Stephenson, G. F. *J. Org. Chem.* **1965**, *30*, 2791–2798.
(13) Stanienda, A.; Biebl, G. *Z. Phys. Chem. (Frankfurt am Main)*, **1967**, *52*, 254–275. See also ref 11.
(14) Johnson, E. C.; Dolphin, D. *Tetrahedron Lett.* **1976**, 2197–2200.
(15) Shine, H. J.; Ristagno, C. V. *J. Org. Chem.* **1971**, *36*, 4050–4055.
(16) Bonnett, R., Gale, I. A. D.; Stephenson, G. F. *J. Chem. Soc. C* **1966**, 1600–1604.
(17) Wilk, M.; Bez, W.; Rochlitz, J. *Tetrahedron* **1966**, *22*, 2599–2608. Rochlitz, J. *Ibid.* **1967**, *23*, 3043–3048. Johnson, M. D.; Calvin, M. *Nature (London)* **1973**, *241*, 271–272.

(18) Svanholm, U.; Parker, V. D. *Acta Chem. Scand.* **1973**, *27*, 1454–1456.
(19) Padilla, A. G.; Wu, S. M.; Shine, H. J. *J. Chem. Soc., Chem. Commun.* **1976**, 236–237.
(20) Evans, B.; Smith, K. M.; Cavaleiro, J. A. S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 768–773.
(21) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworth: London, 1965.
(22) Chakrabarty, M. R.; Handloser, C. S.; Mosher, M. W. *J. Chem. Soc., Perkin Trans. 2* **1973**, 938–942.
(23) Besecke, S.; Evans, B.; Barnett, G. H.; Smith, K. M.; Fuhrhop, J.-H. *Angew. Chem.* **1976**, *88*, 616.
(24) Koyama, K.; Susuki, T.; Tsutsumi, S. *Tetrahedron Lett.* **1965**, 627–630.
(25) Nilsson, S. *Acta Chem. Scand.* **1973**, *27*, 329–335.
(26) Shine, H. J.; Ristagno, C. V. *J. Org. Chem.* **1972**, *37*, 3424–3426.
(27) Inhoffen, H. H. Fuhrhop, J.-H., Voigt, H.; Brockmann, H. *Justus Liebigs Ann. Chem.* **1966**, *695*, 133–143.
(28) Grigg, R.; Shelton, G.; Sweeney, A.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1789–1799.
(29) Fanning, J. C.; Gray, T. L. *J. Chem. Soc., Chem. Commun.* **1974**, 23–24.
(30) Wittig, G.; Geissler, G. *Justus Liebigs Ann. Chem.* **1953**, *580*, 44–57.
(31) Maercker, A., *Org. React.* **1965**, *14*, 270–490.
(32) Clezy, P. S.; Fookes, C. J. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1268.
(33) Bonnett, R.; Charalambides, A. C.; Martin, R. A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 974–980.
(34) (a) Jackson, A. H.; Kenner, G. W.; McGillivray, G.; Smith, K. M. *J. Chem. Soc. C* **1968**, 294–302. (b) Barnett, G. H.; Hudson, M. F.; McCombie, S. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 691–696.
(35) Cavaleiro, J. A. S.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2149–2155.
(36) Evans, B.; Smith, K. M. *Tetrahedron* **1977**, *33*, 629–633.
(37) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 349–363.
(38) Cox, M. T.; Howarth, T. T.; Jackson, A. H.; Kenner, G. W., *J. Am. Chem. Soc.* **1969**, *91*, 1232–1233.
(39) Kochi, J. K.; Bethea, III, T. W. *J. Org. Chem.* **1968**, *33*, 75–82.
(40) E.g., Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 997–1001, 2942–2946.
(41) Abraham, R. J.; Eivazi, F.; Pearson, H.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 698–699, 699–701.
(42) Fuhrhop, J.-H.; Wasser, P.; Reisner, D.; Mauzerall, D. *J. Am. Chem. Soc.* **1972**, *94*, 7996–8001. Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *Ibid.* **1970**, *92*, 3451–3459.
(43) Dolphin, D.; Halko, D. J.; Johnson, E. C.; Rousseau, K. In "Porphyrin Chemistry Advances", Longo, F. R., Ed.; Ann Arbor Press: Ann Arbor, Mich., 1979; pp 119–141.
(44) Fuhrhop, J.-H.; Mauzerall, D. *J. Am. Chem. Soc.* **1969**, *91*, 4174–4181.
(45) Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1471–1475.
(46) Whitlock, H. W.; Hanauer, R. W.; Oester, M. Y.; Bower, B. K. *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489.
(47) Johnson, A. W.; Oldfield, D. *J. Chem. Soc. C* **1965**, 4303–4312.

A Unified Mechanism for Thermal and Photochemical Activation of Charge-Transfer Processes with Organometals. Steric Effects in the Insertion of Tetracyanoethylene

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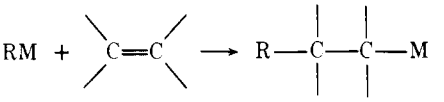
Abstract: Transient absorption bands observed with organometals and the common electron acceptor, tetracyanoethylene (TCNE), are shown to arise from 1:1 charge-transfer complexes. The frequency of the charge-transfer band ν_{CT}, as well as the formation constant K_{CT} and extinction coefficient ϵ_{CT}, of weak σ–π complexes derived from a series of homologous tetraalkyltin compounds R_4Sn are sensitive measures of electronic and steric effects, as determined independently by the ionization potentials I_D and the steric parameters of alkyl groups E_s, respectively, of the donor. The disappearance of the charge-transfer (CT) complex follows overall second-order kinetics with rate constant k_T, and it leads to the 1:1 insertion adduct $R_3Sn(TCNE)R$. The same adduct can also be produced with unit quantum yield by the direct irradiation of the charge-transfer band at low temperatures where the thermal reaction does not occur. Steric effects in the formation of the complex (K_{CT}) parallel those in the thermal insertion (k_T). Steric effects are reflected in the photochemical insertion insofar as they influence the energy and oscillator strength of the CT transition as well as the formation constant of the complex. Thermal activation ($\log k_T$) and photochemical activation ($h\nu_{CT}$) of insertion are both associated with an electron-transfer process which proceeds from the charge-transfer complex [R_4Sn TCNE] to form the same paramagnetic ion pair [$R_4Sn^+ \cdot TCNE^- \cdot$]. Thermal and photochemical processes also share common intermediates subsequent to activation by electron transfer. Thus, in both, insertion follows from a series of rapid, dark reactions involving the stepwise collapse of the ion pair [$R_4Sn^+ \cdot TCNE^- \cdot$] by (1) the spontaneous fragmentation of the $R_4Sn^+ \cdot$ moiety akin to that observed in the gas phase upon electron impact, followed by (2) radical recombination and ion pairing all within the solvent cage. The nature of the ion pair is probed by examining selectivities in mixed methylethyltin compounds for Me–Sn and Et–Sn insertions. The alkyl and TCNE radical pair, that is, [$R \cdot R_3Sn^+$ $TCNE^- \cdot$], is shown to be the prime intermediate by quantum-yield measurements for their simultaneous formation during the irradiation of the charge-transfer band in a frozen matrix at −175 °C. No CIDNP could be observed during thermal activation of insertion.

Introduction

Organometals are involved as reactants or intermediates in a variety of synthetic organic procedures and catalytic processes. As electron-rich species, they are generally subject to cleavage by acids, metal complexes, and other electrophiles.[1] Furthermore, alkylmetals can have rather low ionization potentials, and electron-transfer mechanisms are also possible in which the rate is limited by the ability of the organometal to function as an electron donor and the electrophile to be an electron acceptor.

Tetracyanoethylene (TCNE) has been widely used as an electron acceptor in charge transfer spectral studies, particularly with organic π donors.[2] Donor–acceptor interactions with TCNE have been reported for a few organometallic σ donors.[3-6] The charge-transfer bands for organometals RM are generally weak, and more interestingly they are transient, leading to the simple 1:1 adduct, i.e.



RM + C=C → R—C—C—M (1)

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