Transition-Metal-Catalyzed Cyclization of [*a*,*c*]Biladiene Salts as an Efficient Route to the Synthesis of Alkyl Porphyrins

TRISTANO BOSCHI, ROBERTO PAOLESSE and PIETRO TAGLIATESTA*

Dipartimento di Scienze e Tecnologie Chimiche, II Università degli Studi di Roma 'Tor Vergata', 00173 Rome (Italy)

(Received August 2, 1989)

Abstract

Several alkyl porphyrins have been synthesized by cyclization of different 1,19-dimethyl[*a*,*c*]biladiene dihydrobromides, catalyzed by rhodium, ruthenium and chromium salts in buffered alcoholic media. When the reactions were carried out without base, a drastic reduction of porphyrin yields was observed. No substantial differences were observed on changing the solvent. A different reaction pathway was seen when the 1,19-substituent groups were bulkier than methyl.

Introduction

The cyclization reactions of 1,19-dimethyl[*a*,*c*]-biladiene, carried out in the presence of chromium, rhodium and ruthenium salts in buffered ethanolic solution, give the corresponding porphyrin free base. The yields depend both on the nature of the biladiene and on the metal ion and are comparable or higher than those reported in the literature. No significant improvements are obtained when *N*,*N*-dimethylformamide (DMF) is used as reaction solvent. When the reactions are carried out with copper(II) acetate in buffered ethanolic solution, we obtained a significant improvement of the yields, but the reaction products were the corresponding copper(II) porphyrinates.

Different alkyl groups at the 1,19-positions on biladiene have a strong influence on the reaction: when either ethyl or 2-methoxycarbonylethyl groups are present, the general effect is a decrease in the yields of porphyrins and a different reaction pattern. In fact, if Cr or Rh salts are used as catalysts only etioporphyrin II is obtained, probably via recombination of dipyrromethene fragments derived from the fission of the biladiene.

*Author to whom correspondence should be addressed.

Experimental

NMR were recorded on a Bruker WP 80 SY instrument as $CDCl_3$ solutions with tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as dichloromethane solutions. Mass spectra were measured on a Balzer QMG 511 spectrometer. Melting points were measured on a hot-stage apparatus and are uncorrected. All solvents were Reagent grade and were used without further purification.

Ethyl-5-acetyl-3,4-dimethylpyrrole-2-carboxylate

Ethyl-3,4-dimethylpyrrole-2-carboxylate (10 g) and acetyl chloride (20 ml) were added to a suspension of $AlCl_3$ (64 g) in dry dichloromethane (500 ml), under nitrogen at room temperature. The mixture was stirred for 3 h, then poured into the water. After three extractions with dichloromethane and evaporation of the solvent, the residue was crystallized from benzene/hexane (1:1) to give white crystals (38 g, 75%), melting point 101–102 °C. ^{1}H NMR: 9.43 (1H, s, NH), 4.35 (2H, q, CH_2CH_3), 2.49 (3H, s, $COCH_3$), 2.29 (6H, s, CH_3), 1.37 (3H, t, CH_2CH_3).

Ethyl-5-ethyl-3,4-dimethylpyrrole-2-carboxylate

The above pyrrole (11 g) was dissolved in dry benzene (300 ml) under nitrogen in a Dean–Stark apparatus and tosylhydrazine (11.2 g) and *p*-toluensulfonic acid (100 mg) were added. The mixture was refluxed and the water removed. Sodium cyanoborohydride (8 g) was added under reflux and after 12 h the mixture was hydrolyzed with dilute hydrochloric acid and extracted with diethyl ether. The solvent was evaporated under vacuum and the residue was chromatographed on silica gel eluting with diethyl ether/hexane (1:1). Crystallization from hexane afforded the pure product (8.2 g, 80%), melting point 64–65 °C. ^{1}H NMR: 8.72 (1H, s, NH), 4.30 (2H, q, $CO_2CH_2CH_3$), 2.63 (2H, q, CH_2CH_3), 2.26 (3H, s, CH_3), 1.93 (3H, s, CH_3), 1.35 (3H, t, $CO_2CH_2CH_3$), 1.2 (3H, t, CH_2CH_3).

0020-1693/90/$3.50

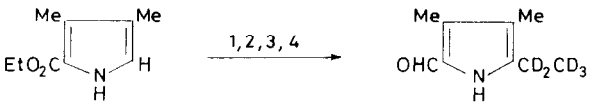
5-Ethyl-3,4-dimethylpyrrole-2-carbaldehyde

The above pyrrole (22 g) was dissolved in water/ethanol (1:1) (200 ml) with KOH (60 g) and refluxed for 4 h. After evaporation of ethanol under vacuum, the alkaline solution was cooled to 0 °C and neutralized with dilute hydrochloric acid. The pyrrole-2-carboxylic acid was filtered off, washed with water, dried and then dissolved in trifluoroacetic acid (20 ml) under nitrogen. After 10 min the solution was poured into the water and extracted with diethyl ether; after evaporation of the solvent, the viscous oil was formylated by the literature method [1].

Elution on silica gel with diethyl ether/hexane (1:1) afforded the pyrrole 2-carbaldehyde (3.6 g, 34%), melting point 65–67 °C. ^{1}H NMR: 10.12 (1H, b, NH), 9.49 (1H, s, CHO), 2.60 (2H, q, CH_2CH_3), 2.25 (3H, s, CH_3), 1.90 (3H, s, CH_3), 1.22 (3H, t, CH_2CH_3).

5-[$^2H_5$]Ethyl-3,4-dimethylpyrrole-2-carbaldehyde

This pyrrole was prepared by the same experimental procedure as described above and represented in Scheme 1. Physical properties were the same as the corresponding pyrroles reported above.



Scheme 1. Reagents: 1, CD_3COCl; 2, tosyl hydrazide/$NaBD_4$; 3, $NaOH/H_2O$; 4, $POCl_3$/DMF.

4-(2-Methoxycarbonylethyl)-3,5-dimethylpyrrole-2-carbaldehyde

Benzyl-4-(2-methoxycarbonylethyl)-3,5-dimethylpyrrole-2-carboxylate [2] (10 g) was dissolved in tetrahydrofuran (THF) (250 ml) and hydrogenated at room temperature over palladium charcoal (1 g) until uptake of hydrogen ceased. The catalyst was removed by filtration through Celite and the filtrate was evaporated under vacuum; the pyrrole-2-carboxylic acid was dissolved in trifluoroacetic acid (30 ml) and stirred for 10 min under nitrogen; the mixture was cooled to 0 °C before addition of trimethyl orthoformate (60 ml). The mixture was stirred for 10 min, poured into the water (1 l) and extracted twice with dichloromethane. The organic extract was washed with a water solution of sodium hydrogen carbonate, dried and evaporated under vacuum. The residue was chromatographed on silica gel, eluting with diethyl ether/hexane 1:1, to afford the pyrrole-2-carbaldehyde (4 g, 60%), melting point 123–125 °C. ^{1}H NMR: 9.46 (1H, s, CHO), 3.65 (3H, s, CO_2CH_3), 2.54 (4H, m, $-CH_2CH_2-$), 1.09 (6H, s, CH_3).

Benzyl-5-formyl-3,4-dimethylpyrrole-2-carboxylate

This compound was synthesized from benzyl-3,4,5-trimethylpyrrole-2-carboxylate [3], as reported by Johnson and coworkers [4]. Benzyl-3,4,5-trimethylpyrrole-2-carboxylate (24.4 g) was dissolved in 500 ml of glacial acid and $Pb(CH_3COO)_4$ (44.4 g) was added over about 1 h. When the lead tetraacetate had dissolved, a further quantity (44.4 g) was added and the mixture was warmed at 90 °C on a water bath with stirring for 1 h, then poured into ice-water (1 l) and refrigerated. The product was collected after 12 h and crystallized from absolute ethanol to give colorless plates (21.2 g, 82%), melting point 119–120 °C. ^{1}H NMR: 9.66 (1H, s, CHO), 7.29 (5H, s, Ph), 5.24 (2H, s, CH_2Ph), 2.18 (6H, s, CH_3).

Benzyl-5-(2-carboxymethylvinyl)-3,4-dimethylpyrrole-2-carboxylate

The above pyrrole (20 g) and trimethylphosphonoacetate (28 g) in THF (100 ml) were added to a well-stirred solution of potassium hydroxide (5 g) in THF (150 ml) under nitrogen at room temperature. After 24 h the mixture was diluted with diethyl ether and washed with water (3 × 100 ml), dried and evaporated. The product was crystallized from dichloromethane–hexane to give white crystals (20.2 g, 83%) melting point 173–175 °C. ^{1}H NMR: 9.08 (1H, b, NH), 7.63 (1H, d, $-CH{=}CHCO_2CH_3$), 7.43 (5H, s, Ph), 6.12 (1H, d, $-CH{=}CHCO_2CH_3$), 5.38 (2H, s, CH_2Ph), 3.82 (3H, s, CO_2CH_3), 2.30 (3H, s, CH_3), 2.14 (3H, s, CH_3).

5-(2-Methoxycarbonylethyl)-3,4-dimethylpyrrole-2-carbaldehyde

The above pyrrole (20.2 g) was hydrogenated over palladium charcoal (2 g) at room temperature until uptake of hydrogen ceased. The catalyst was removed by filtration through Celite and the filtrate was evaporated to give the pyrrole carboxylic acid which was treated with trifluoroacetic acid (20 ml) and trimethyl orthoformate (30 ml). The mixture was stirred for 10 min, poured into water (500 ml) and extracted with dichloromethane (2 × 150 ml); the organic layer was washed with aqueous sodium hydrogen carbonate, dried and evaporated to dryness. The product was crystallized from THF–hexane to give the title compound (8 g, 64%); melting point 88–90 °C. ^{1}H NMR: 9.50 (1H, s, CHO), 3.69 (3H, s, CO_2CH_3), 2.73 (4H, m, $-CH_2CH_2-$), 2.24 (3H, s, CH_3), 1.94 (3H, s, CH_3).

Biladienes

The [*a*,*c*]biladiene dihydrobromide salts were prepared by the previously reported method [5] from the appropriate dipyrromethane-5,5′-dicarboxylic acid [6] and the corresponding pyrrole-2-carbaldehyde. The spectral data are as follows.

1,2,3,7,8,12,13,17,18,19-Decamethyl[a,c]-biladiene dihydrobromide (1)

UV (λ, nm): 450, 526. ^{1}H NMR: 13.25, 13.14 (each 2H, b, NH), 7.07 (2H, s, =CH–), 5.15 (2H, s, CH_2), 2.67, 2.27, 2.20, 1.99, 1.89 (each 6H, s, CH_3).

8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyl-[a,c]biladiene dihybrobromide (2)

UV (λ, nm): 452, 528. ^{1}H NMR: 13.42, 13.22 (each 2H, b, NH), 7.10 (2H, s, =CH–), 5.18 (2H, s, CH_2), 2.58 (4H, q, CH_2CH_3), 2.68, 2.32, 2.24, 1.98 (each 6H, s, CH_3), 0.78 (6H, t, CH_2CH_3).

8,12-Diethyl-2,18-bis(2-methoxycarbonylethyl)-1,3,7,13,17,19-hexamethyl[a,c]biladiene dihydrobromide (3)

UV (λ, nm): 452, 527. ^{1}H NMR: 13.38, 13.25 (each 2H, b, NH), 7.11 (2H, s, =CH–), 5.20 (2H, s, CH_2), 3.67 (6H, s, CO_2CH_3), 2.71, 2.31, 2.23 (each 6H, s, CH_3), 2.56–2.47 (12H, m, $-CH_2CH_2-$ and CH_2CH_3), 0.65 (6H, t, CH_2CH_3).

1,8,12,19-Tetraethyl-2,3,7,13,17,18-hexamethyl-[a,c]biladiene dihydrobromide (4)

UV (λ, nm): 452, 532. ^{1}H NMR: 13.32, 13.18 (each 2H, b, NH), 7.10 (2H, s, =CH–), 5.22 (2H, s, CH_2), 3.08, 2.54 (8H, q, CH_2CH_3), 2.27, 2.20, 2.18 (each 6H, s, CH_3), 1.24, 0.82 (12H, t, CH_2CH_3).

1,19-[$^2H_{10}$]Diethyl-8,12-diethyl-2,3,7,13,17,18-hexamethyl[a,c]biladiene dihydrobromide (5)

This biladiene has the same spectral data as **4**, but in the ^{1}H NMR spectrum the resonances at 3.08 and 1.24 of deuterated ethyl groups disappear.

1,19-Bis(2-methoxycarbonylethyl)-8,12-diethyl-2,3,7,13,17,18-hexamethyl[a,c]biladiene dihydrobromide (6)

UV (λ, nm): 455, 530. ^{1}H NMR: 13.42, 13.26 (each 2H, b, NH), 7.12 (2H, s, =CH–), 5.22 (2H, s, CH_2), 3.68 (6H, s, CO_2CH_3), 3.26–2.54 (12H, m, CH_2CH_2 and CH_2CH_3), 2.28, 2.20, 2.12 (each 6H, s, CH_3), 0.82 (6H, t, CH_2CH_3).

1,2,18,19-Tetrakis(2-methoxycarbonylethyl)-8,12-diethyl-3,7,13,17-tetramethyl[a,c]biladiene dihydrobromide (7)

UV (λ, nm): 454, 530. ^{1}H NMR: 13.51, 13.20 (each 2H, b, NH), 7.15 (2H, s, =CH–), 5.23 (2H, s, CH_2), 3.67, 3.65 (each 6H, s, CO_2CH_3), 3.34–2.47 (20H, m, CH_2CH_2 and CH_2CH_3), 2.31, 2.23 (each 6H, s, CH_3), 0.70 (6H, t, CH_2CH_3).

Cyclizations of Biladienes in Ethanol

The [a,c]biladiene dihydrobromide (100 mg) was added to a solution of sodium acetate (500 mg) and metal salt (100 mg) in 95% ethanol (100 ml). The green solution was refluxed under aereation for 4 h and the color turned to red–brown. After evaporation of the ethanol, the residue was extracted with dichloromethane and chromatographed on silica gel (elution with dichloromethane) to give the corresponding porphyrins. In the case of the biladiene **1** and **2**, the porphyrin crystallized in the reaction mixture and was filtered off to give the analytically pure product.

If other oxidants were used, the reactions were carried out under nitrogen and the residue was treated as described above.

Cyclizations of Biladienes in DMF

The [a,c]biladiene dihydrobromide (100 mg) was added to a suspension of metal salt in DMF (50 ml) and then a few drops of triethylamine were added. The green solution was refluxed for 1 h, then the solvent was evaporated under vacuum and the residue was treated as above.

Yields of porphyrins are reported in Table 1, structural formulae are reported in Fig. 1 for biladienes and Fig. 2 for porphyrins.

TABLE 1. Cyclizations of [a,c]bidentate dihydrobromides (BD) with metal salts

BD	Metal salt	Solvent	Porphyrin yield (%)
1	$Cr(OAc)_3$	EtOH	51
		DMF	40
	$RhCl_3$	EtOH	46
		DMF	<5[a]
	$RuCl_3$	EtOH	32
	$Cu(OAc)_2$	EtOH	80
2	$Cr(OAc)_3$	EtOH	60
		DMF	35
	$RhCl_3$	EtOH	43
		DMF	<5[a]
	$RuCl_3$	EtOH	30
	$Cu(OAc)_2$	EtOH	90
3	$Cr(OAc)_3$	EtOH	42
	$RhCl_3$	EtOH	29
	$Cu(OAc)_2$	EtOH	65
4	$Cr(OAc)_3$	EtOH	28[b]
	$RhCl_3$	EtOH	19[b]
	$Cu(OAc)_2$	EtOH	45[c]
5	$Cr(OAc)_3$	EtOH	25[b]
	$RhCl_3$	EtOH	20[b]
6	$Cr(OAc)_3$	EtOH	20[b]
	$RhCl_3$	EtOH	11[b]
7	$Cr(OAc)_3$	EtOH	9[b]
	$RhCl_3$	EtOH	<5[b]

[a]Porphyrinato Rh-methyl; [b]etioporphyrin II; [c]3,17-diethyl-2,8,12,13,15,17,18-heptamethylporphyrin.

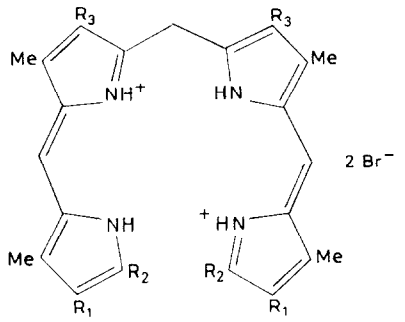


Fig. 1. Biladienes: $R_1 = R_2 = R_3 = Me$ (1); $R_1 = R_2 = Me$, $R_3 = Et$ (2); $R_1 = P$, $R_2 = Me$, $R_3 = Et$ (3); $R_1 = Me$, $R_2 = R_3 = Et$ (4); $R_1 = Me$, $R_2 = D$, $R_3 = Et$ (5); $R_1 = Me$, $R_2 = P$, $R_3 = Et$ (6); $R_1 = R_2 = P$, $R_3 = Et$ (7); $P = CH_2CH_2COOCH_3$; $D = CD_2CD_3$.

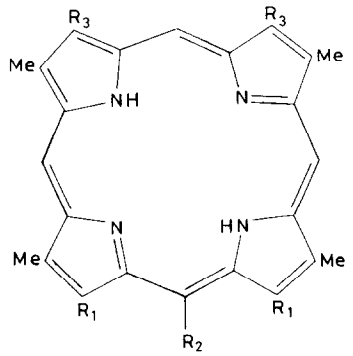


Fig. 2. Porphyrins: $R_1 = R_3 = Me$, $R_2 = H$ (8); $R_1 = Me$; $R_2 = H$, $R_3 = Et$ (9); $R_1 = P$, $R_2 = H$, $R_3 = Et$ (10); $R_1 = R_3 = Et$, $R_2 = H$ (11); $R_1 = R_2 = Me$, $R_3 = Et$ (12).

Results and Discussion

The cyclization of [*a*,*c*]biladiene salts catalyzed by copper(II) ions has proved to be one of the most successful syntheses of porphyrins [7]. The reactions were generally carried out in DMF and the products were the corresponding copper(II) porphyrinates [7]. A great number of porphyrins of biological interest have now been synthesized by this method and several studies have been performed in order to determine the general mechanism of the cyclization and to optimize the yields of porphyrins [8–12].

Nevertheless, such a procedure suffers from some disadvantages, such as the unpredictable yields of porphyrins that sometimes have been reported to be discouraging, and the production of copper porphyrinates. In fact, if acid-labile substituents are present on the macrocycles, the removal of the metal ion can be quite difficult.

In order to overcome such problems we thought of chosing different systems that would allow the formation of the porphyrin free base in good yield. Ni(II) and Co(II) salts have been discarded because they afford, under the same conditions, the corresponding metal tetradehydrocorrin salts [4]. During our studies on the chemistry of tetrapyrrolic macrocycles we have found [13] that Cr(III), Ru(III) and Rh(III) catalyze the cyclization of 1,19-unsubstituted [*a*,*c*]-biladiene salts to give metal-free corrole.

In the present work the same metal ions have been used in the cyclization of several 1,19-dialkyl [*a*,*c*]-biladienes, the formulae of which are reported in Fig. 1. These [*a*,*c*]biladiene salts have been prepared according to literature methods [5] from the appropriate 2-pyrrolecarbaldehyde and the dipyrromethane 5,5′-dicarboxylic acid. The successive cyclizations of [*a*,*c*]biladienes have been generally carried out using ethanol as solvent with an excess of sodium acetate in the presence of air. When methyl groups are present at the 1,19-positions of the [*a*,*c*]biladiene salts, the corresponding *meso*-unsubstituted metal-free porphyrins have been obtained.

The general interest and the great advantage of these new reactions is the direct synthesis of porphyrin free bases and the elimination of the harsh acidic conditions necessary for the removal of the chelated copper atom. The synthesis of macrocycles with acid-labile substituents, which is an usual condition for biological-like compounds, is then allowed.

The yields of the reactions are also higher than those reported in the literature and are summarized in Table 1. The yields are dependent on both the [*a*,*c*]-biladienes and the metal ions used and have been found to be optimal when Cr(III) acetate and 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyl [*a*,*c*] biladiene dihydrobromide (**2**) have been employed, leading to the formation of 3,7-diethylhexamethylporphyrin in 60% yield.

In order to optimize the yields of the cyclization reactions, some experimental details, such as the nature of oxidants and base, have been varied. The use of triethylamine instead of sodium acetate does not influence the reaction pathway, while the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or $K_2Cr_2O_7$ as oxidants, always in the presence of Cr(III) ions, although it did not improve the yields increased the reactions rates.

When the cyclization was carried out using DMF as solvent, the reaction pathway was found to be strongly dependent on the metal ion. The variation of solvent in the presence of Cr(III) acetate did not influence the nature of the porphyrin free base obtained, but only the reaction yield, which was lower, whilst when $RhCl_3$ was used, we obtained in very low yield (<5%) a mixture of Rh porphyrinates, where the predominant compound was the Rh-methyl porphyrinato. This results can be ascribed to the well-known reactivity of rhodium trichloride with alkyl amides [14].

In order to compare the reactivity of different metal ions, we have performed the same reaction using Cu(II) acetate and obtained the corresponding Cu porphyrinates. The yields are always higher than those obtained with the other metal salts and are improved with respect to those reported in the literature for similar cyclizations [15]. Furthermore, when compound **2** is used, the yield is almost quantitative (90%). These enhancements are probably due to the presence of the excess of base. In fact, if the reaction is carried out without sodium acetate, a drastic reduction of porphyrin yields is observed. The presence of the base drives the reaction towards the deprotonation of biladiene which is considered to be the first step of the cyclization [16].

When the 1,19-positions of the biladienes were occupied by alkyl groups different from methyl, we obtained different results. When 1,8,12,19-tetraethyl-2,3,7,13,17,18-hexamethyl[*a*,*c*]biladiene dihydrobromide (**4**) was refluxed in ethanol with Cr(III) acetate or $RhCl_3$, surprisingly only etioporphyrin II was obtained and *meso*-substituted porphyrins were not isolated. Under the same conditions, Cu(II) acetate affords *meso*-methylporphyrin, thus indicating a different pathway of cyclization.

In order to elucidate the mechanism of this reaction, we have synthesized the 1,19-[$^2H_5$]diethyl-8,12-diethyl-2,3,7,13,17,18-hexamethyl[*a*,*c*]biladiene dihydrobromide (**5**). The [*a*, *c*]biladiene can be prepared by literature methods and the relative [$^2H_5$]pyrrolecarbaldehyde is achieved by the procedure reported in Scheme 1.

Cyclization carried out with Cr(III) acetate or $RhCl_3$ afforded etioporphyrin II and no incorporation of deuterium was observed. This result seems to indicate that the cyclization is no longer achieved by the oxidation of the terminal alkyl group. Cr and Rh salts probably cause fission of the bilatriene, formed in the buffered solution, at the terminal methine bridge and afford etioporphyrin II by the recombination of two dipyrromethene fragments. A similar result was observed by Johnson and Kay in the cyclization of [*b*]bilenes catalyzed by $AlCl_3$ [17].

This pathway is confirmed by the reaction with 1,19-bis(2-methoxycarbonylethyl)-8,12-diethyl-2,3,7,13,17,18-hexamethyl[*a*,*c*]biladiene dihydrobromide (**6**), 1,2,18,19-tetrakis(2-methoxycarbonylethyl)-8,12-diethyl-3,7,13,17-tetramethyl[*a*,*c*]biladiene dihydrobromide (**7**): using these biladienes we have always obtained the etioporphyrin II in lower yields.

When DMF is used as solvent in the cyclization of compound **4**, Cr(III) acetate afforded etioporphyrin II and *meso*-methylporphyrin in lower yield. A possible explanation for the formation of the *meso*-substituted porphyrin comes from the use of a high boiling solvent such as DMF. The temperature probably allows the overcoming of the energy barrier necessary for the cyclization and the *meso*-methylporphyrin is then formed.

Further research directed towards the isolation of the intermediates and the optimization of the yields in the cyclization catalyzed by Cr, Rh or Ru salts is in progress.

References

1 G. M. Badger, R. L. N. Harris and R. A. Jones, *Aust. J. Chem., 17* (1964) 1022.
2 H. Furhop and K. M. Smith, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins,* Elsevier, New York, 1975.
3 A. W. Johnson, E. Markham, R. Price and K. B. Shaw, *J. Chem. Soc.*, (1958) 4254.
4 D. Dolphin, R. L. N. Harris, J. Huppatz, A. W. Johnson and I. T. Kay, *J. Chem. Soc. C,* (1966) 30.
5 R. B. Woodward, *Pure Appl. Chem., 2* (1961) 383.
6 (a) H. Fischer and B. Walach, *Annalen, 450* (1926) 109; (b) E. Bullock, A. W. Johnson, E. Markham and K. B. Shaw, *J. Chem. Soc.*, (1958) 1430.
7 A. W. Johnson, in D. Dolphin (ed.), *The Porphyrins,* Vol. 1, Part A, Academic Press, New York, 1978, Ch. 5, and refs. therein.
8 J. A. B. Almeida, G. W. Kenner, K. M. Smith and M. J. Sutton, *J. Chem. Soc., Chem. Commun.*, (1975) 111.
9 K. M. Smith, K. C. Lagry and O. M. Minnetian, *J. Org. Chem., 49* (1984) 4602.
10 R. Grigg, A. W. Johnson, R. Kenyion, V. B. Math and K. Richardson, *J. Chem. Soc. C,* (1969) 176.
11 K. M. Smith and O. M. Minnetian, *J. Org. Chem., 50* (1985) 2073.
12 K. M. Smith, K. M. Snow and D. Jeyakumar, *J. Am. Chem. Soc., 110* (1988) 8562.
13 T. Boschi, S. Licoccia, R. Paolesse and P. Tagliatesta, *J. Chem. Soc., Dalton Trans.*, (1989), in press.
14 T. Boschi, S. Licoccia and P. Tagliatesta, *Inorg. Chim. Acta, 143* (1988) 235.
15 (a) K. M. Smith and O. M. Minnetian, *J. Chem. Soc., Perkin Trans.*, (1986) 277; (b) K. M. Smith, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins,* Elsevier, New York, 1975.
16 D. Dolphin, A. W. Johnson, J. Leng and P. van den Broek, *J. Chem. Soc., C,* (1966) 880.
17 A. W. Johnson and I. T. Kay, *J. Chem. Soc. C,* (1961) 2418.