

## Condensation of Ethyl Diazoacetate with Cobalt Porphyrins

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Condensation of ethyl diazoacetate with various cobalt complexes of octaethylporphyrin causes insertion of ethoxycarbonylcarbene into a cobalt–nitrogen bond to give a salt (VI) of the cobalt(III) adduct. Reduction of the salt (VI) with chromium(II) salts causes the formation of neutral halogenocobalt(II) complexes of *N*-ethoxycarbonylmethyloctaethylporphyrin, e.g. (XIII). The action of acid under oxidative conditions on (VI) yields first a halogenocobalt(II) *N*-ethoxycarbonylhalogenomethyloctaethylporphyrin (XI), and then, after removal of the metal, 21,22-ethoxycarbonylmethyleneoctaethylporphyrin, the first example of a *cis*-21,22-bridged porphyrin. The parent 21,22-methyleneoctaethylporphyrin is obtained by condensation of di-iodomethane with octaethylporphyrin.

EARLY considerations of the mechanism of the biochemical rearrangements controlled by cobalamin-containing enzymes<sup>1</sup> included the possibility that a cobalt carbene complex is an intermediate in the reactions. Such complexes were unknown at that time<sup>2</sup> and it was of interest to ascertain whether cobalt porphyrins would react with a suitable carbene. We describe here the reactions of cobalt(II) octaethylporphyrin (I; M = Co, R = H) and corresponding cobalt(III) complexes with ethyl diazoacetate.

We have shown<sup>3</sup> that copper(II) octaethylporphyrin and ethyl diazoacetate give a mixed product which, after removal of the metal, yields a small amount of the *meso*-substituted porphyrin (I; M = H<sub>2</sub>, R = CH<sub>2</sub>·CO<sub>2</sub>-Et), together with larger quantities of the isomeric chlorins (II; R<sup>1</sup> = H, R<sup>2</sup> = CO<sub>2</sub>Et; R<sup>1</sup> = CO<sub>2</sub>Et, R<sup>2</sup> = H). Elimination of nitrogen from aliphatic diazo-compounds is known<sup>4</sup> to be catalysed by copper compounds, and it is probable that the adducts (II) are formed by reaction of ethoxycarbonylcarbene with the cross-conjugated double bonds of the copper porphyrin. The stereochemistry of the isomeric adducts related to (II), but obtained from reaction of zinc(II) *meso*-tetraphenylporphyrin with ethyl diazoacetate in the presence of copper salts,

has been examined by Callot,<sup>5</sup> who also isolated the bis-adducts (III) and the product (IV) formed by reaction of the carbene at one of the porphyrin nitrogen atoms.<sup>6</sup>

In the cobalt series, initial experiments were carried out with cobalt(II) octaethylporphyrin and ethyl diazoacetate in dichloromethane or chloroform.<sup>7</sup> The reaction was catalysed by traces of hydrogen chloride and at room temperature was complete (colour change; u.v.) after 15 min and gave *ca.* 64% of the major product. Reaction with bromo(pyridine)cobalt(III) octaethylporphyrin<sup>8</sup> was faster (*ca.* 3 min) and gave *ca.* 60% of mixed products, and condensation with cobalt(III) octaethylporphyrin bromide was extremely fast (<0.1 min) and gave *ca.* 80% of the major product. No other metal porphyrin examined has reacted nearly so rapidly as this cobalt(III) derivative with ethyl diazoacetate. Because the reaction is favoured by electron depletion at the metal, it is thought to involve 1,3-dipolar addition of ethyl diazoacetate with subsequent loss of nitrogen rather than addition of the electrophilic carbene.

When the reaction mixtures were quenched with light petroleum immediately on completion of the reaction,

<sup>5</sup> H. J. Callot, *Bull. Soc. chim. France*, 1972, 4387; *Tetrahedron*, 1973, **29**, 899.

<sup>6</sup> H. J. Callot and T. Tschamber, *Bull. Soc. chim. France*, 1973, 3192.

<sup>7</sup> Preliminary communication, P. Batten, A. L. Hamilton, A. W. Johnson, G. Shelton, and D. Ward, *J.C.S. Chem. Comm.*, 1974, 550.

<sup>8</sup> A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1960, 2979.

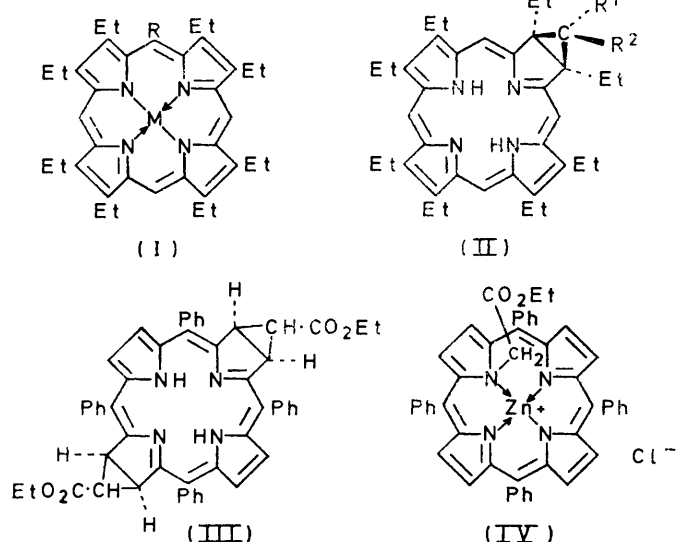
<sup>1</sup> R. H. Abeles, personal communication.

<sup>2</sup> D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

<sup>3</sup> H. J. Callot, A. W. Johnson, and A. Sweeney, *J.C.S. Perkin I*, 1973, 1424.

<sup>4</sup> W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

in each case a moderately stable dark purple cobalt-containing chloride (electrophoresis, conductivity) was isolated as the major product, but smaller quantities of two isomeric neutral cobalt-containing compounds formed by condensation of one mole of cobalt octaethylporphyrin



with two moles of ethyl diazoacetate, as well as the acid transformation product (XI) (see below) were identified. After longer periods of reaction and with greater quantities of ethyl diazoacetate, the 1 : 2 neutral condensation compounds were formed as the major products. Their structures will be discussed in a later paper.

Solutions of the chloride in polar solvents were brown and decomposed slowly to a mixture of products including cobalt(II) octaethylporphyrin, but the microcrystalline chloride could be obtained by chromatography on a column of polycaprolactam (polyamide) and repeated rapid crystallisation from methylene chloride–light petroleum. Decomposition of solutions of the salt was accelerated by heat or by the presence of bases or an excess of acid. The solid salt was moderately stable in light in spite of the presence of the cobalt–carbon bond (see below), but decomposition to cobalt(II) octaethylporphyrin occurred on irradiation of a solution in dichloromethane with visible light for 12 h. In the cobalamin series, electron-attracting substituents are known to stabilise the cobalt–carbon bond towards photolysis.

The chloride was formulated as  $C_{40}H_{50}ClCoN_4O_2$ , corresponding to a 1 : 1 addition product with loss of nitrogen, on the basis of analysis and i.r. and mass spectra. The mass spectrum was complicated by the fission and recombination of multiple carbene fragments with the molecular ion at the probe. However a weak (1%) ion was observed at  $m/e$  677 corresponding to  $C_{40}H_{50}CoN_4O_2$  (loss of chloride) and a base peak at  $m/e$  591 [cobalt(II) octaethylporphyrin]. In the electronic spectrum a marked diminution in intensity of the Soret band compared with those of the cobalt porphyrins suggested that

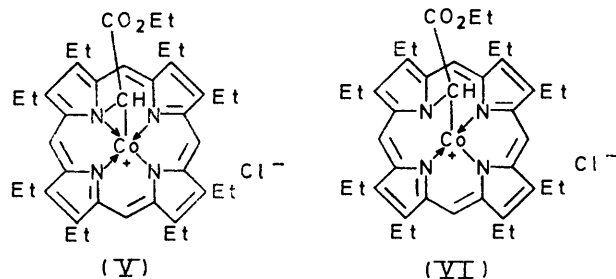
<sup>9</sup> Professor T. J. King, personal communication.

the symmetry of the original porphyrin had been appreciably reduced in the product.

Polarographic examination (see Table) of the chloride showed two distinct one-electron steps and suggested a cobalt(III) complex. The difference of *ca.* 0.5 V in the  $E_{\frac{1}{2}}$  values for the first reduction step of the chloride and that of cobalt(III) octaethylporphyrin bromide reflects the difference in the type of bonding at the metal. Polarographic oxidation proceeded only with difficulty and led to decomposition, and a controlled potential reduction of the salt at  $-0.7$  V in the absence of added halide produced cobalt(II) octaethylporphyrin (76%).

From a solution of the chloride in  $[^2H]$ chloroform an informative n.m.r. spectrum was obtained at  $-35$  °C. The spectrum showed that all four porphyrin *meso*-protons were still present (four separate singlets between  $\tau$   $-0.23$  and  $+0.13$ ) and that the eight  $\beta$ -ethyl groups remained substituents at  $sp^2$  carbon atoms. Hence, unlike the copper<sup>3</sup> and zinc<sup>5,6</sup> porphyrins, reaction of the cobalt porphyrins with ethyl diazoacetate had involved neither *meso*-substitution nor  $\beta$ -addition. The spectrum also showed a high field triplet at  $\tau$  10.38 ( $CO_2 \cdot CH_2 \cdot CH_3$ ), indicating the shielding effect on the ester by the porphyrin ring current, and a singlet at  $\tau$  11.78 ( $CH \cdot CO_2Et$ ). The  $^{13}C$  (natural abundance) n.m.r. spectrum of the corresponding bromide in deuteriochloroform at 0 °C showed four separate signals for the four *meso*-carbon atoms. The carbonyl carbon signal was associated with a singlet at  $\delta$  167.821 and the methine carbon possibly with another singlet at  $\delta$  22.630.

An assessment of the above evidence led us<sup>7</sup> to propose (V) as the structure of the primary adduct, which is formed by insertion of the carbenoid fragment into the metal–nitrogen bond, a type of reaction which has not

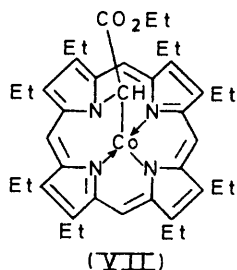


been reported previously.<sup>2</sup> However an *X*-ray examination<sup>9</sup> of one of the neutral isomers, a 2 : 1 ethyl diazoacetate–cobalt porphyrin adduct, formed by double insertion into porphyrin Co–N bonds (above) or by reaction of more ethyl diazoacetate with the initially formed chloride, has shown that the distance between the carbene-substituted nitrogen and the cobalt atom is 2.7 Å, thus precluding the existence of the co-ordinate bond. Our suggested structure for the initially formed chloride has therefore been modified from (V) to (VI), although as yet it has not been possible to produce a crystal of (VI) suitable for *X*-ray examination. In considering the mechanism of formation of (VI) from cobalt(II) octaethylporphyrin we have shown by polarography that the neutral cobalt(II) reduction product (VII) of (VI) is

unstable in solution, having a half-life of *ca.* 2 s. Nevertheless it seemed that in the reaction of cobalt(II) octaethylporphyrin with ethyl diazoacetate ester, (VII) could have been an intermediate in the formation of (VI), which it would give by oxidation. However, the reaction was shown to occur over 1 h in an atmosphere of oxygen-free nitrogen although the yield (*ca.* 30%) of product was lower. It was also shown that the gaseous products from the reaction consisted only of nitrogen, uncontaminated with hydrogen (the metal might have been oxidised at the expense of hydrogen chloride, derived from solvent), and consequently under anaerobic conditions the cobalt(III) product was formed by disproportionation. In view of the increased yield (*ca.* 64%) of product obtained when the condensation is carried out in presence of air, it seems that aerial oxidation is an alternative mechanism for formation of the cobalt(III) complex. The oxidative step is of course unnecessary in the reactions with cobalt(III) porphyrins and the higher yields (*ca.* 80%) observed are therefore as expected.

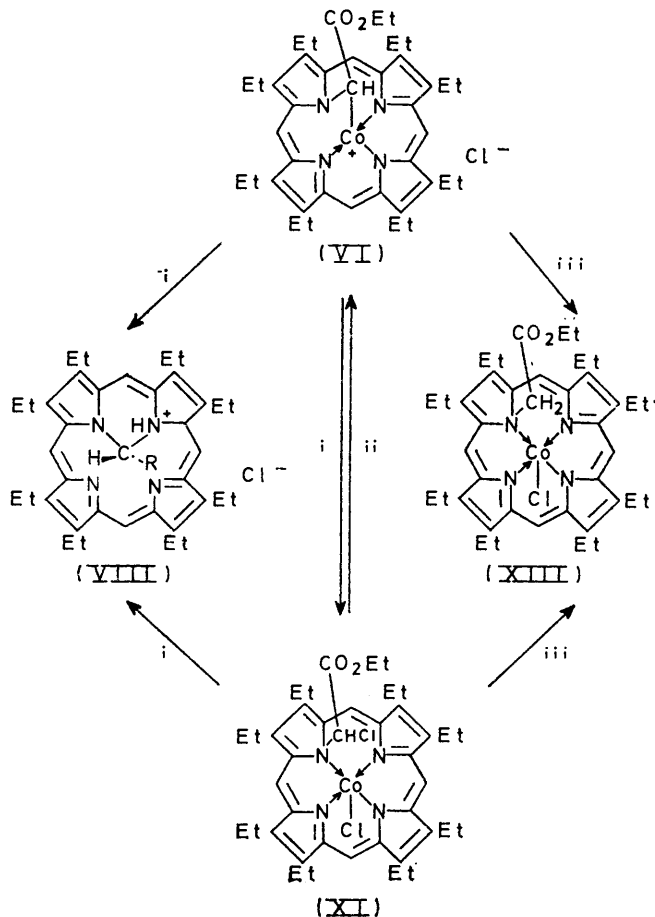
Further support for structure (VI) for the primary adduct of ethyl diazoacetate and cobalt octaethylporphyrin has been obtained from a study of its chemical reactions, summarised in Scheme 1. The integrity of the carbene in (VI) was demonstrated by heating an ethanolic solution of the salt under reflux in presence of sodium acetate: diethyl fumarate mixed with a little diethyl maleate (*cf.* ref. 10) was isolated from the volatile fraction and cobalt(II) octaethylporphyrin was also obtained. Attempts to trap the carbene by carrying out the reaction in the presence of cyclohexene or cyclo-octa-1,5-diene were unsuccessful, however. Reductions of solutions of the salt in tetrahydrofuran with either sodium borohydride or sodium amalgam also gave cobalt(II) octaethylporphyrin.

Thus, in order to retain the carbenoid fragment in transformations of (VI) it was necessary to maintain mild



acidic conditions and to avoid elevated temperatures. Treatment of the salt (VI) with ethanolic 10% hydrogen chloride at room temperature gave two products, a dichroic orange-green neutral compound containing both cobalt and chlorine, dilute solutions of which were bright green, and a reddish purple cobalt-free chloride. This chloride could be obtained from the neutral compound by treatment with more acid and also from the original salt (VI) by treatment with an excess of ethanolic hydrogen chloride at room temperature. Crystallisation of the chloride from acetone-sodium bromide gave the bromide,  $C_{40}H_{51}BrN_4O_2$  (analysis, mass spectrum); the

corresponding perchlorate was also prepared. The salts were stable and each showed a strong Soret band in the



SCHEME 1 Reagents: i, EtOH-HCl; ii,  $CrCl_2-Et_3N$  or chromatography on  $SiO_2$ ; iii,  $CrCl_2-HCl$

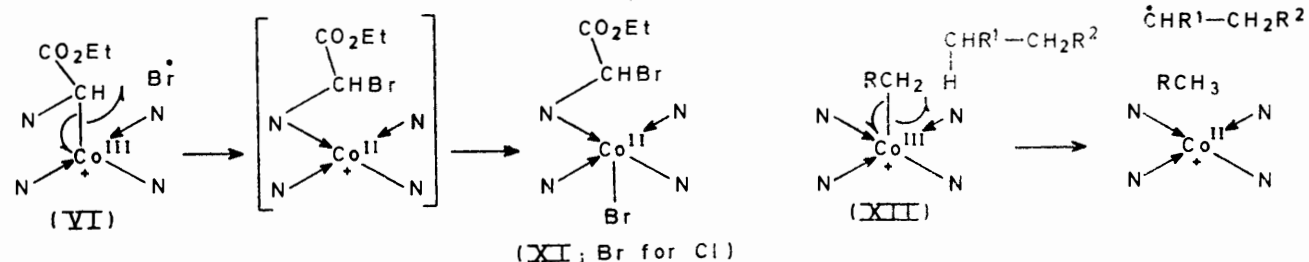
visible spectrum. The n.m.r. spectrum of the chloride showed the signals for the four *meso*-protons in a 1 : 2 : 1 singlet pattern and also the methine proton signal as a singlet at  $\tau$  15.78. The product has therefore been formulated as (VIII;  $R = CO_2Et$ ), which constitutes the first example of a 21, 22-*cis*-bridged porphyrin; the alternative 21,23-*cis*-bridged structure would have shown the *meso*-proton signals in a 2 : 2 pattern. Introduction of the carbon atom between N-21 and N-22 completes a new six membered ring and the resulting structure is therefore relatively free from strain. The methine proton in (VIII;  $R = CO_2Et$ ) was exchangeable with deuterium (with  $D_2O$  at room temperature), presumably owing to its location between the ester group and the charged nitrogen atom. In an n.m.r. spectrum of a solution of the chloride in  $[^2H]$ chloroform the imino-proton signal was not observed at room temperature, but at  $-55^\circ C$  was seen as a broad resonance at  $\tau$  11.85. In the perchlorate, the imino-proton showed a very broad signal at room temperature at  $\tau$  11.90. The free base from (VIII;  $R = CO_2Et$ ) was formed in solution during chromatography of the hydrochloride on alumina or by

<sup>10</sup> R. K. Armstrong, *J. Org. Chem.*, 1966, **31**, 618.



where the initial stage is the homolytic cleavage of the cobalt(III)-carbon bond, which is followed by hydrogen abstraction from the substrate<sup>14</sup> [rather than combina-

ponding bromo- and iodo-derivatives was obtained by use of the appropriate sodium halide in the crystallisation. The acetate of cobalt(II) *N*-methyloctaethylporphyrin



$RCH_2 \equiv 5'$ -deoxyadenosyl  
 $R^1 = OH, R^2 = NH_2$ , for example

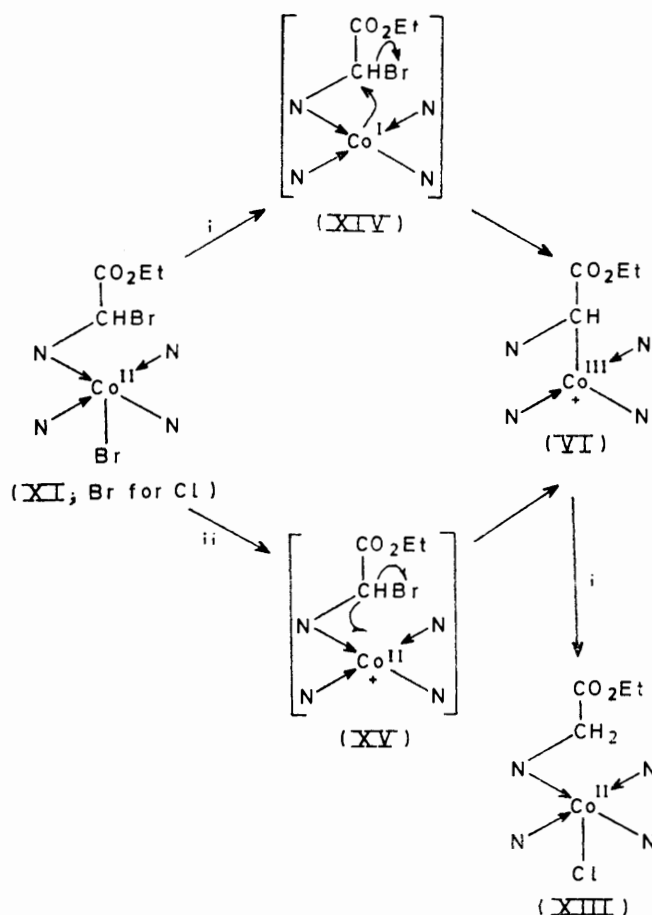
SCHEME 2

tion with the bromine atom as in the formation of (XI; Br for Cl)].

Conditions have also been established for the reverse change (XI)  $\rightarrow$  (VI). Reduction of (XI; Br for Cl) with chromium(II) bromide gave the bromocobalt(II) 21-ethoxycarbonylmethyloctaethylporphyrin analogue (XIII; Br for Cl) (9.8%) (*i.e.* CHBr  $\rightarrow$  CH<sub>2</sub>) and cobalt(II) octaethylporphyrin (22%) as well as the bromide of (VI) (18.7%). The formation of (VI) from (XI) under reductive conditions may well involve the intermediacy of a cobalt(I) species [*e.g.* (XIV)]; such species are known<sup>15</sup> to react readily with alkyl halides to give alkylcobalt(III) derivatives. It is possible that the reduction of (XI) to (XIII) also proceeds by way of (VI) (Scheme 3), as this transformation is known to be brought about by chromium(II) salts (see below). Cobalt(II) octaethylporphyrin and the bromide of (VI) were also obtained from (XI; Br for Cl) during prolonged chromatography on silica; a radical process (XV) probably operates in this case. Similar reactions with the dichloro-complex (XI) were slower than with the dibromo-analogue.

Treatment of the salt (VI) with concentrated sulphuric acid at 0 °C for 30 min gave a mixture of a little *N*-ethoxycarbonylmethyloctaethylporphyrin (XVI) (see below) and octaethylporphyrin itself. Reduction of a solution of the salt (VI) with chromium(II) chloride (or bromide) in ethanolic hydrochloric acid gave cobalt(II) *N*-ethoxycarbonylmethyloctaethylporphyrin as the crystalline pentaco-ordinate chloro- (or bromo-) derivative (XIII). The neutral character of the product was indicated by electrophoresis and conductivity studies and the divalent nature of the metal by polarography, from which evidence for both one-electron oxidation and reduction was obtained. The structural assignment was supported by its molecular weight (vapour pressure osmometer), magnetic moment measurements (high spin Co<sup>II</sup> complex), and finally an X-ray examination.<sup>13</sup> Ready halogen exchange was demonstrated by t.l.c. experiments and evidence for the existence of the corres-

has been described recently<sup>16</sup> and shown to rearrange to methylcobalt(III) octaethylporphyrin during reduction



SCHEME 3 Reagents: i, CrCl<sub>2</sub>; ii, prolonged chromatography on SiO<sub>2</sub>

with sodium borohydride. We have prepared cobalt(II) *N*-methyloctaethylporphyrin iodide.

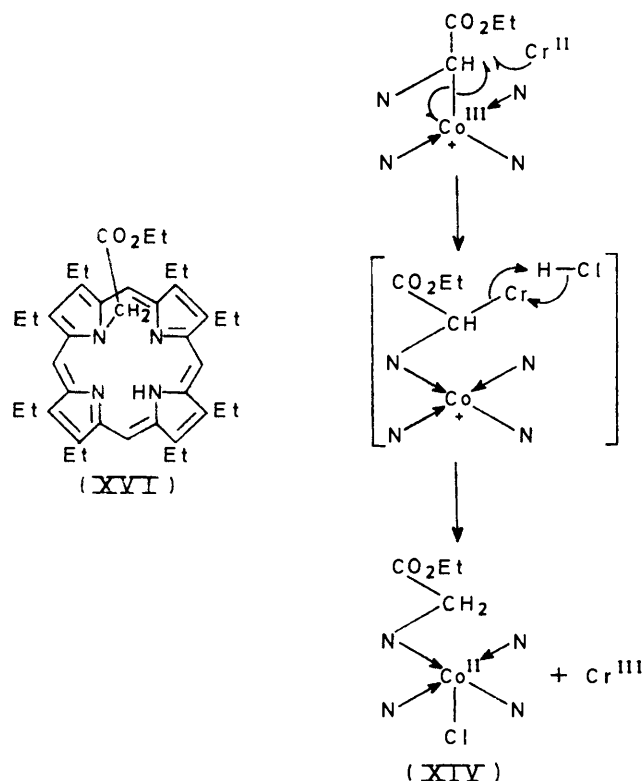
Demetallation of (XIII) with 10% ethanolic hydrogen

<sup>14</sup> H. Ogoshi, E. Watanbe, N. Koetsu, and Z. Yoshida, *J.C.S. Chem. Comm.*, 1974, 943.

<sup>14</sup> H. A. Barker, *Ann. Rev. Biochem.*, 1972, **41**, 55.

<sup>15</sup> A. W. Johnson, L. Mervyn, N. Shaw, and E. Lester Smith, *J. Chem. Soc.*, 1963, 4146.

chloride yielded *N*-ethoxycarbonylmethyloctaethylporphyrin (XVI); the structure of the corresponding hydride has been defined by X-ray crystallography.<sup>17</sup> The n.m.r. spectrum contained a sharp signal at  $\tau$  14.02



SCHEME 4

corresponding to the *N*-methylene grouping. Treatment of octaethylporphyrin with ethyl bromoacetate (*cf.* ref.

cobalt into (XVI) presented no difficulty and the product was identical with the product (XIII) of reduction of (VI) with chromium(II) chloride. Reaction of cobalt(II) octaethylporphyrin with ethyl bromoacetate yielded no useful product.

The mechanism of the reductive cobalt-carbon bond cleavage of alkylcorrins by chromium(II) salts is thought to involve alkylchromium intermediates as depicted in Scheme 4.<sup>18</sup> The conversion of (VI) into (XIII) was also carried out electrolytically in the presence of 1 equiv. of hydrochloric acid or of an excess of chloride. However attempts to reverse the process [*i.e.* (XIII)  $\rightarrow$  (VI)] by electrochemical or chemical oxidation were unsuccessful: only cobalt(III) octaethylporphyrin chloride was obtained.

**Polarography and Cyclic Voltammetry.**—As reference compounds, cobalt(II) octaethylporphyrin [Co<sup>II</sup>OEP], cobalt(III) octaethylporphyrin bromide, and the radical-cation of the latter produced<sup>12</sup> by oxidation with bromine were examined, and these showed one, two, and three reduction steps respectively. This method thus provided valuable evidence as to the nature of the cobalt in the various transformation products. Results are summarised in the Table and also included for comparison are the properties of the known cobalt(II) *N*-methyloctaethylporphyrin iodide (see Experimental section).

#### EXPERIMENTAL

N.m.r. spectra were measured for solutions in [<sup>2</sup>H]chloroform and u.v.-visible spectra for solutions in chloroform (except where otherwise stated) with instruments listed in earlier papers in this series. Mass spectra were determined by direct sample insertion into the ion source of an A.E.I. MS9 instrument. The <sup>13</sup>C n.m.r. spectrum was determined at 25.15 MHz (JEOL PFT-100 spectrometer with proton

Half-wave potentials and peak potentials of cobalt porphyrin derivatives \*

Complex	$E_{\frac{1}{2}}$ † and/or $E_p$ ‡ (V)		Behaviour §	
	Reduction	Oxidation	Reduction	Oxidation
Co <sup>II</sup> OEP	−1.00	+0.47, +0.93	Rev.	Q-Rev.; Rev.
[Co <sup>III</sup> OEP] <sup>+</sup> Br <sup>−</sup>	+0.01, −1.05	+0.90	Q-Rev.; Rev.	Rev.
[Co <sup>III</sup> OEP] <sup>2+</sup> Br <sub>2</sub> <sup>−</sup>	+0.53, −0.10, −0.98		Rev.; Q-Rev.; Rev.	
(VI)	−0.49, −1.08	+1.05	Rev.; Rev.	Irrev.
(XI)	−0.99	+0.96	Rev.	Irrev.
(XI; Br for Cl)	−0.92		Rev.	
(XIII)	−0.83	+0.92		Irrev.
[Co <sup>II</sup> <i>N</i> -Me-OEP] <sup>+</sup> I <sup>−</sup>	−0.83	+0.63	Irrev.	Irrev.

\* Solvent dichloromethane–20% methanol (except for [Co<sup>III</sup> OEP]<sup>2+</sup> Br<sub>2</sub><sup>−</sup> and (XIII) for which the methanol was omitted as a chemical interaction occurred), 0.1N in tetraethylammonium fluoroborate; solutions *ca.* 1mM in complex and saturated with argon. †  $E_{\frac{1}{2}}$  Values are half-wave potentials measured by polarography at a dropping mercury electrode. ‡  $E_p$  values are italicised and are peak potentials of cyclic voltammograms (vitreous carbon electrode at scan rate of 30 mV s<sup>−1</sup>); for reversible processes  $E_{\frac{1}{2}}$  precedes  $E_p$  by 29 mV. § Rev.  $\equiv$  reversible process; oxidised and reduced species are interconvertible through a rapid electron transfer process; Q-Rev.  $\equiv$  quasi-reversible process; the electron-transfer step is slower than in the reversible process; Irrev.  $\equiv$  irreversible process; very slow electron-transfer step and the oxidised and reduced forms may not be interconvertible by electron transfer only.

11) gave mainly the *trans*-21,22-bis-*N*-ethoxycarbonylmethyl derivative (X; R = CH<sub>2</sub>CO<sub>2</sub>Et), isolated as the perchlorate, but the best method for the preparation of *N*-ethoxycarbonylmethyloctaethylporphyrin is treatment of the zinc complex with acid.<sup>5,6</sup> Introduction of

<sup>17</sup> G. M. McLaughlin, *J.C.S. Perkin II*, 1974, 136.

<sup>18</sup> J. H. Epenson and T. D. Sellers, *J. Amer. Chem. Soc.*, 1974, 96, 94.

noise decoupling); chemical shifts are reported in p.p.m. downfield from tetramethylsilane. The electrochemical experiments employed the same apparatus as described previously.<sup>19</sup> M.p.s were determined with a Köfler hot-stage apparatus, and magnetic moments with a Faraday balance. Column chromatography was carried out with

<sup>19</sup> C. M. Elson, A. L. Hamilton, and A. W. Johnson, *J.C.S. Perkin I*, 1973, 775.

MN-polyamide CC6 (polycaprolactam) as adsorbent except where otherwise stated, and for t.l.c. experiments Merck pre-coated silica gel plates were used. Chloroform, dichloromethane, and carbon tetrachloride were purified by passage through an activated alumina column prior to use. Light petroleum refers to the fraction of b.p. 60–80°.

**Reaction of Ethyl Diazoacetate with Cobalt Complexes of Octaethylporphyrin.**—(i) *Cobalt(II) octaethylporphyrin.* Ethyl diazoacetate (0.5 ml) was added to cobalt(II) octaethylporphyrin (500.3 mg) in chloroform (40 ml) at room temperature. The mixture was stirred for 20 min during which the colour of the solution changed from red to brown. The solvent was removed, the residue dissolved in chloroform (20 ml), and polycaprolactam (10 g) added. The solvent was again removed and the residue was added to a column (4 × 100 cm) of polycaprolactam and eluted with 0.5% acetone–light petroleum to remove unchanged cobalt octaethylporphyrin (11.7 mg after crystallisation from dichloromethane–methanol). Further elution with 5% acetone–light petroleum gave a mixture of two neutral brown compounds (87.2 mg, 12%) formed by reaction of the cobalt porphyrin with 2 mol. equiv. of ethyl diazoacetate. Increasing the proportion of acetone to 20% gave the green neutral cobalt-containing complex (XI) (see below) (70.6 mg, 11%, after crystallisation from dichloromethane–light petroleum). The major product (VI) was eluted with chloroform–acetone–light petroleum (1 : 1 : 4) and was obtained as brown microcrystals of *NCo-ethoxycarbonylmethylene cobalt(III) octaethylporphyrin chloride* (386 mg, 63.8% after two purifications from dichloromethane–light petroleum) (Found: C, 67.5; H, 7.0; Cl, 5.0; N, 7.4.  $C_{40}H_{50}ClCoN_4O_2$  requires C, 67.7; H, 7.0; Cl, 4.9; N, 7.8%),  $\lambda_{max}$  250, 412, and 516 nm,  $\lambda_{infl}$  550, 572, and 607 nm ( $\epsilon$  12 800, 49 980, 9 320, 8 270, 7 380, and 4 300),  $\nu_{max}$  (KBr) 1 722 (C=O) and 1 210 and 1 190  $cm^{-1}$  (C–O),  $\Lambda$  (in oxygen-free nitrobenzene at room temperature) 16  $cm^2 ohm^{-1} mol^{-1}$ ; paper electrophoresis (3% acetic acid) caused the salt to move 1.2 cm in 30 min at 3 000 V and 24 mA [under these conditions a sample of a cobalt(II) tetrahydrocorrin salt moved similarly but neutral cobalt(II) octaethylporphyrin was immobile];  $\tau$  (room temperature) 0.54 (s, 1 *meso*-H), 1.15 (s, 2 *meso*-H), 1.22 (s, 1 *meso*-H), 5.0–7.0br (8 H, m, 4 × CH<sub>2</sub>), 5.31 (4 H, q, 2 × CH<sub>2</sub>), 6.77 (4 H, q, 2 × CH<sub>2</sub>), 8.2 (26 H, m, 8 × CH<sub>3</sub> and ester CH<sub>2</sub>), and 10.52 (3 H, t, ester CH<sub>3</sub>) (no singlet for the methine proton observed). A similar n.m.r. spectrum was obtained for the corresponding bromide (below). The salt decomposed during chromatography on alumina, silica, or Florisil. It was rapidly decomposed by bases and was unstable in the presence of an excess of acid, but the dried salt could be stored below 0 °C under nitrogen. Solutions of the salt decomposed in a few days.

(ii) *Cobalt(III) octaethylporphyrin bromide.* The cobalt(III) complex (41.6 mg) in chloroform (5 ml) was mixed with ethyl diazoacetate (0.02 ml). A rapid reaction occurred in *ca.* 1 s with a colour change from deep red to brown. The solution was evaporated to small volume under reduced pressure and the residue diluted with light petroleum to precipitate the bromide (VI; Br for Cl) as a purple amorphous solid which was separated and washed with light petroleum. It was purified by dissolution in dichloromethane–light petroleum and concentration to give a brown microcrystalline solid (37.4 mg, 79%) (Found: N, 7.4.  $C_{40}H_{50}BrCoN_4O_2$  requires N, 7.4%). Spectral properties, including n.m.r. in CDCl<sub>3</sub> at room temperature, were similar to those reported for the chloride (above);  $\tau$  (–35 °C) –0.23 (s, 1 *meso*-H),

0.06 (s, 1 *meso*-H), 0.11 (s, 1 *meso*-H), 0.13 (s, 1 *meso*-H), 6.1 (16 H, m, 8 × CH<sub>2</sub>), 8.1 (26 H, m, 8 × CH<sub>3</sub> and ester CH<sub>2</sub>), 10.38 (3 H, t, ester CH<sub>3</sub>), 11.78 (s, 1 methine H);  $\delta_0$  (CDCl<sub>3</sub> at 0 °C) 149.493–142.698 (nuclear C), 146.969 (CH·CO<sub>2</sub>Et), 104.599, 103.966, 100.277, and 95.908 (*meso*-C), 58.730 (O·CH<sub>2</sub>·CH<sub>3</sub>), 20.191–17.813 (nuclear Et), and 12.328 (O·CH<sub>2</sub>·CH<sub>3</sub>).

(iii) *Bromo(pyridine)cobalt(III) octaethylporphyrin.* The cobalt porphyrin<sup>8</sup> (75.3 mg) in chloroform (8 ml) was mixed with ethyl diazoacetate (0.065 ml) and stirred for 5 min. Periodic u.v. examination showed the reaction was complete in 3 min. The mixture was treated as in (ii) and the product (43.4 mg, *ca.* 60%) obtained as a purple precipitate which was washed with light petroleum. T.l.c. showed it to be a mixture of the bromide (VI; Br for Cl).

**Action of Sodium Acetate on the Bromide (VI; Br for Cl).**—The bromide (9 mg) and sodium acetate (50 mg) in ethanol (2 ml) were heated under reflux for 20 min. After cooling, the red solid was separated and crystallised from dichloromethane to give needles of cobalt(II) octaethylporphyrin (3.2 mg, 43%), identical with an authentic specimen.

**Reductions of the Salts (VI) by Chromium(II).**—(i) *Chlorocobalt(II) N-ethoxycarbonylmethyloctaethylporphyrin (XIII).* The chloride (VI); (174.8 mg) was dissolved in dichloromethane (10 ml) in an atmosphere of nitrogen. A solution of chromium(II) chloride<sup>20</sup> (3 ml; 0.15M-CrCl<sub>2</sub> in ethanol) was added to the solution by syringe inserted through a sealed rubber cap, and the mixture was stirred for 5 min; a colour change from brown to reddish brown occurred. The mixture was poured into aqueous saturated sodium hydrogen carbonate (200 ml) and extracted with dichloromethane (3 × 100 ml). The combined extracts were washed, dried, and concentrated and the product was then chromatographed on polycaprolactam. After a preliminary elution with 3% acetone–light petroleum to remove impurities, the main product was eluted with 20% acetone–light petroleum. After removal of solvent, the *chlorocobalt complex* was separated and crystallised from acetone–1% aqueous sodium chloride to give purple needles (114.9 mg, 65.6%), m.p. 257° (decomp) (Found: C, 67.6, H, 7.2; Cl, 5.3; N, 8.0.  $C_{40}H_{51}ClCoN_4O_2$  requires C, 67.3; H, 7.2; Cl, 4.9; N, 7.8%),  $\lambda_{max}$  311, 382, 426, 542, 585, and 617  $nm$  ( $\epsilon$  15 500, 47 380, 94 760, 7 750, 11 120, and 3 870),  $\nu_{max}$  1 754 (C=O), 1 194, 1 170 and 1 117  $cm^{-1}$  (C–O),  $\mu_{eff}$  5.1 B.M. [high-spin cobalt(II)],  $\Lambda$  (in oxygen-free nitrobenzene at room temperature) 1.8  $cm^2 ohm^{-1} mol^{-1}$  (*cf.* the parent bromide,  $\Lambda$  16  $cm^2 ohm^{-1} mol^{-1}$ ); in 3% acetic acid, the product showed no movement on paper electrophoresis at 3 000 V and 24 mA; *m/e* 715.4 (33.1%, *M* + 1), 714.3 (42.6%, *M*), 713.4 (100%, *M* – 1), and 591.5 [11.7%, cobalt(II) octaethylporphyrin] by field desorption method.

(ii) *Bromocobalt(II) N-ethoxycarbonylmethyloctaethylporphyrin.* The bromide (VI; Br for Cl) (226 mg) was reduced with chromium(II) bromide in a manner similar to that used for the chloride and the bromocobalt complex (XIII; Br for Cl) was similarly purified. It formed violet prisms (120.7 g, 53%) (Found: C, 63.5; H, 6.9; N, 7.6.  $C_{40}H_{51}BrCoN_4O_2$  requires C, 63.6; H, 6.8; N, 7.4%),  $\lambda_{max}$  311, 386  $nm$ , 426, 540, 586, 607, and 619  $nm$  ( $\epsilon$  12 850, 42 500, 81 300, 6 640, 8 700, 4 310, and 2 930),  $\nu_{max}$  1 756 (C=O), 1 192, and 1 176  $cm^{-1}$  (C–O), *m/e* 760.5 (15%, *M* + 1), 759.5 (35.9%, *M* for <sup>81</sup>Br), 758.5 (13.8%, *M* – 1 for <sup>81</sup>Br and *M* + 1 for <sup>79</sup>Br), 757.4 (30.2%, *M* for <sup>79</sup>Br), and 591.5 [11.7%, cobalt(II) octaethylporphyrin].

<sup>20</sup> J. R. Hanson, *Synthesis*, 1974, 1.

*Demetallation of Chlorocobalt(II) N-Ethoxycarbonylmethyloctaethylporphyrin.*—The chloro-compound (26 mg) was dissolved in ethanolic 10% hydrogen chloride (25 ml) at room temperature and stirred for 1 h; the colour of the solution changed from green to blue-purple. The product was poured into aqueous saturated sodium carbonate (1 l) and extracted with dichloromethane (3 × 40 ml). The solvent removed from the combined organic extracts and the residue subjected to preparative t.l.c. on silica (15% acetone-dichloromethane). The reddish brown band was separated, the product extracted with acetone, and the solvent removed. The residue was crystallised from dichloromethane-methanol to give purple prisms of (XVI) (17 mg; 74%), identical with the product obtained (below) by demetallation of (VI) with concentrated sulphuric acid.

*Demetallation of the Ethyl Diazoacetate-Cobalt(II) Octaethylporphyrin Adduct (VI)*—The chloride (VI) (313 mg) was dissolved in concentrated sulphuric acid (50 ml) at 0 °C with shaking. Hydrogen chloride was evolved from the blue solution. After 30 min the solution was cautiously poured into excess of cold aqueous ammonium carbonate and the porphyrins were then extracted into methylene chloride. The combined extracts were washed with water, the solvent was removed, and the residue was purified by preparative t.l.c. on silica (30% acetone-methylene chloride). The faster running fraction was octaethylporphyrin (43 mg, 18.3%, from methylene chloride-methanol) and the other fraction was *N-ethoxycarbonylmethyloctaethylporphyrin* (XVI) (63.2 mg, 23.3%), obtained after crystallisation from methylene chloride-light petroleum, as purple cubes, m.p. 233–235° (Found: C, 77.4; H, 8.2; N, 9.1.  $C_{40}H_{52}N_4O_2$  requires C, 77.4; H, 8.4; N, 9.0%),  $\lambda_{max}$  407, 501, 533, 581, and 633 nm ( $\epsilon$  101 000, 7 700, 7 000, 4 000, and 2 500),  $\nu_{max}$  3 310 (NH) and 1 741  $cm^{-1}$  (C=O),  $m/e$  620, ( $M$ , 10%),  $\tau$  0.16 (2 *meso*-H), 0.28 (2 *meso*-H), 6.0 (16 H, m, 8 × peripheral  $CH_2$ ), 7.15 (2 H, q, ester  $CH_2$ ), 8.0 (18 H, m, 6 × peripheral  $CH_3$ ), 8.33 (6 H, t, 2 × peripheral  $CH_3$ ), 9.5 (3 H, t, ester  $CH_3$ ), 13.3br (s, NH), and 14.02 (2 H, s,  $N-CH_2$ ; no exchange with  $D_2O$ ), identical with that obtained by demetallation (above) of its chlorocobalt(II) complex.

The chlorocobalt(II) complex (XIII) was formed (67%) by reaction of *N-ethoxycarbonylmethyloctaethylporphyrin* (20.1 mg) with cobalt(II) acetate (22.0 mg) in methanol at room temperature for 1 h. Purification of the product including crystallisation from acetone-1% aqueous sodium chloride gave the product as purple needles, identical with the product formed by reduction of the chloride (VI) with chromium(II) chloride.

*Cobalt(II) N-Methyloctaethylporphyrin Iodide.*—*N-Methyloctaethylporphyrin* <sup>15</sup> (100 mg) in chloroform (50 ml) was treated with cobalt(II) chloride (100 mg) in methanol (50 ml) and the mixture heated under reflux for 15 min. The solvent was evaporated off and the residue chromatographed on alumina [chloroform-methanol (9 : 1)]. The main band was eluted and the eluate shaken with aqueous potassium iodide and then water. After removal of the solvent, the product was crystallised from chloroform-hexane to give purple needles (125 mg, 87%) (Found: C, 60.8; H, 6.85.  $C_{37}H_{47}CoI_2$  requires C, 60.6; H, 6.45%).

*Bromocobalt(II) N-Bromo(ethoxycarbonyl)methyloctaethylporphyrin (XI; Br for Cl).*—(i) The bromide (VI; Br for Cl) (270.6 mg) was dissolved in dichloromethane (10 ml) and a solution (1 ml) of bromine (0.01 ml) in carbon tetrachloride (10 ml) was added. The mixture was stirred for 50 min; after 15 min the colour changed from brown to green. Most

of the solvent was removed under reduced pressure at room temperature and the residue was adsorbed on polycaprolactam (8 g) and then added to a column (2 × 75 cm) of polycaprolactam. Some impurities were removed by elution with 2% acetone-light petroleum and the product was eluted with 20% acetone-light petroleum. Removal of the solvent gave a purple solid which was crystallised twice from acetone-light petroleum to give purple needles (166.6 mg; 55.7%) of the *bromocobalt(II) complex* (Found: C, 61.6; H, 6.6; N, 7.2.  $C_{40}H_{50}Br_2CoN_4O_2$  requires C, 61.7; H, 6.5; N, 7.2%),  $[\alpha]_D^{20} 0^\circ$  ( $c$  0.2),  $\lambda_{max}$  311, 388, 433, 442 *infl*, 547, 605, and 641 *infl* nm ( $\epsilon$  16 750, 47 300, 63 200, 58 850, 6 350, 10 680, and 2 310),  $\nu_{max}$  (KBr) 1 762 (C=O), 1 165, 1 150, and 1 113  $cm^{-1}$  (C-O);  $\nu_{max}$  ( $CH_2Cl_2$ ) 1 759  $cm^{-1}$  (C=O),  $\mu_{eff}$  4.7 B.M. [high-spin cobalt(II) complex],  $\Lambda$  (in deoxygenated nitrobenzene at room temperature) 6.3  $cm^2$   $ohm^{-1} mol^{-1}$  (*cf.* original bromide, 16  $cm^2$   $ohm^{-1} mol^{-1}$ ). The e.s.r. spectrum at liquid  $N_2$  temperature showed a single signal with  $g$  2.0011.

(ii) A solution of the bromide (VI; Br for Cl) (65.2 mg) in ethanol (5 ml) was stirred with hydrobromic acid (48%; 0.05 ml) for 5 h at room temperature. The product was treated as in the previous experiment and the green fraction from the chromatography on polycaprolactam was collected and converted into the purple crystalline product (40.9 mg, 56.8%), identical with that obtained in the previous experiment.

When the above experiment was carried out in an atmosphere of nitrogen with solvents which had been freed from oxygen, no reaction was observed (t.l.c.) even when a 1 : 10 molar ratio of bromide salt to acid was used.

(iii) Freshly prepared cobalt(III) octaethylporphyrin dibromide (109.2 mg)<sup>12</sup> was dissolved in dichloromethane (20 ml) and ethyl diazoacetate (0.1 ml) was added. An immediate reaction occurred accompanied by a colour change from dark green to light green. The mixture was treated as in the previous experiments and the main product obtained as purple needles (79.5 mg, 65.3%), shown to be bromocobalt(II) *N-bromo(ethoxycarbonyl)methyloctaethylporphyrin*, identical with that obtained in the previous experiments. A little of the bromide (VI; Br for Cl) was also identified (t.l.c.) in the products.

*Chlorocobalt(II) N-Chloro(ethoxycarbonyl)methyloctaethylporphyrin (XI).*—The chloride (VI) (378.8 mg) was dissolved in acetone (17 ml), concentrated hydrochloric acid (0.2 ml) was added, and the mixture was stirred vigorously for 5–6 h during which time the original brown colour changed to green. The product was worked up in the same manner as the bromo-analogue (above), including chromatography on polycaprolactam. The main green fraction was separated and crystallised from acetone-light petroleum to give purple prisms (301.1 mg, 75.9%) (Found: N, 7.4.  $C_{40}H_{50}Cl_2CoN_4O_2$  requires N, 7.4%),  $\lambda_{max}$  313, 386, 432, 441 *infl*, 548, 606, and 638 nm ( $\epsilon$  13 780, 47 250, 73 500, 68 920, 6 990, 11 030, and 2 660),  $\nu_{max}$  1 763 (C=O), 1 165, 1 151, and 1 116 (C-O)  $cm^{-1}$ .

*Reaction of Bromocobalt(II) N-Bromo(ethoxycarbonyl)methyloctaethylporphyrin with Sulphuric Acid.*—The porphyrin (XI; Br for Cl) (29.3 mg) was dissolved in concentrated sulphuric acid (20 ml) and stirred at room temperature for 10 h. The resulting deep purple solution was poured into water (200 ml) and neutralised with saturated aqueous sodium carbonate. The porphyrins were extracted with dichloromethane (3 × 100 ml) and the organic layer was washed and reduced in volume; then ethanol was added. Small purple crystals of octaethylporphyrin (4.1 mg) soon



formed and were separated. Solvent was removed from the filtrate and the residue was chromatographed on silica gel (preparative t.l.c.) with dichloromethane for elution. More octaethylporphyrin (14.7 mg; total yield 90%) and a salt of its *N*-ethoxycarbonylmethyl derivative (XVI) (1 mg) were isolated.

**Reduction of Bromocobalt(II) *N*-Bromo(ethoxycarbonyl)methyl-octaethylporphyrin with Chromium(II) Bromide.**—The porphyrin (XI; Br for Cl) (216.9 mg) was dissolved in dichloromethane (25 ml) and triethylamine (1 drop) was added. The solution was saturated with nitrogen and sealed in a flask with a rubber septum cap. A solution of chromium(II) bromide (1.8 ml; prepared as in ref. 20 with zinc amalgam as reducing agent) was transferred to the flask by means of a syringe and the mixture stirred for 15 min. The solvent was then removed *in vacuo* and the residue dissolved in a little dichloromethane and adsorbed on polycaprolactam, which was then introduced onto a polycaprolactam chromatography column and eluted with 1% acetone–light petroleum to remove cobalt(II) octaethylporphyrin (33.8 mg, 22%). Further elution with 15% acetone–light petroleum gave a mixture of two green products (see below) and finally elution with chloroform–acetone–light petroleum (1 : 1 : 4) yielded the bromide (VI; Br for Cl) (36.7 mg, 18.7%), which was purified as described above and was then identical with the sample obtained by condensation of ethyl diazoacetate and cobalt(III) octaethylporphyrin bromide.

The mixture of the two green products was separated by preparative t.l.c. on silica (10% acetone–light petroleum) to give bromocobalt(II) *N*-ethoxycarbonylmethyl-octaethylporphyrin (XIII; Br for Cl) (19.1 mg, 9.8%), purified by crystallisation from acetone–1% aqueous sodium bromide. It was identical with the product of reduction of the bromide (VI; Br for Cl) with chromium(II) bromide (see above). The other green product was starting material, which was converted by silica successively into the bromide (VI; Br for Cl) (below) and cobalt(II) octaethylporphyrin.

**Transformations of Bromocobalt(II) *N*-Bromo(ethoxycarbonyl)methyl-octaethylporphyrin on Silica.**—The porphyrin (29.7 mg) was dissolved in dichloromethane (2 ml) and applied as a narrow band to a preparative t.l.c. plate of silica (20 cm<sup>2</sup>; 0.75 mm thick). The plate was repeatedly (6 ×) developed in the presence of added potassium bromide (8% acetone–chloroform as eluant) and dried. The product was then extracted from the silica with acetone, and polycaprolactam (0.7 g) was added. After removal of the acetone, the absorbed product was introduced onto a column of polycaprolactam (14 g; 30 × 1.5 cm) and eluted with light petroleum to remove cobalt(II) octaethylporphyrin (7.7 mg after crystallisation from chloroform–methanol). Starting material (9.1 mg) was eluted with 10% acetone–light petroleum and a further fraction as a brown band was eluted with chloroform–acetone–light petroleum (1 : 1 : 4). The solvent was removed from this fraction and the residue dissolved in dichloromethane (5 ml) and diluted with light petroleum; a dark purple powder was obtained (6.8 mg), the electronic spectrum and t.l.c. behaviour of which were identical with those of the bromide (VI; Br for Cl). Qualitative experiments showed that these transformations of (XI) were accelerated by bases, e.g. sodium methoxide, and that the dichloro-compound decomposed more slowly than the dibromo-compound.

**21,22-Ethoxycarbonylmethyleneoctaethylporphyrin (VIII; R = CO<sub>2</sub>Et).**—(i) The chloride (VI) (313 mg) dissolved in the minimum amount of dichloromethane was added to

10% hydrogen chloride in dry ethanol (30 ml) and the solution was stirred for 2 h; the brown colour changed to dark green. The product was poured into an excess of saturated sodium hydrogen carbonate solution and then extracted into dichloromethane. The extract was washed, dried, and evaporated to give a purple-red solid which was purified by preparative t.l.c. on silica (40% acetone–benzene). The main fraction was crystallised from acetone–aqueous sodium bromide to yield the purple *hydrobromide* (Found: C, 68.85; H, 7.4; Br, 11.3; N, 8.3. C<sub>40</sub>H<sub>51</sub>BrN<sub>4</sub>O<sub>2</sub> requires C, 68.65; H, 7.35; Br, 11.4; N, 8.0%), λ<sub>max</sub> 239, 297, 395, 525, 555, and 598 nm (ε 46 000, 11 200, 160 000, 7 500, 10 400, and 6 200) ν<sub>max</sub> 1 184, 1 215 (C–O), and 1 755 cm<sup>-1</sup> (C=O), τ -0.73 (s, 2 *meso*-H), -0.46 and -0.11 (both 2, each 1 *meso*-H), 5.75 (16 H, m, 8 × nuclear CH<sub>2</sub>·CH<sub>3</sub>), 8.0 (24 H, m, 8 × CH<sub>2</sub>·CH<sub>3</sub>) 8.44 (2 H, q, ester CH<sub>2</sub>·CH<sub>3</sub>), 10.5 (3 H, t, ester CH<sub>2</sub>·CH<sub>3</sub>), and 15.78 (s, methine H, exchangeable with D<sub>2</sub>O) (no imino-signals); electrophoresis on paper (3% in dilute acetic acid) caused a movement of 1.1 cm in 30 min at 3 000 V and 24 mA (confirming that the product was a salt); Λ (nitrobenzene at 25 °C) 24.5 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>; *m/e* 618 (*M*, 82%).

The hydrochloride was converted into the free base by the action of triethylamine or during t.l.c. on alumina; λ<sub>max</sub> 396, 419, 524, 553, 586, 600inf, and 633 nm. Attempted isolation of the free base was thwarted by the ease with which it reverted to its salts.

(ii) Bromocobalt(II) *N*-bromo(ethoxycarbonyl)methyl-octaethylporphyrin (XI; Br for Cl) (32.3 mg) was dissolved in ethanol (15 ml), concentrated hydrochloric acid (0.1 ml) was added, and the solution was stirred for 5 h at room temperature during which the colour changed from bright green to purple-green. The reaction was followed by t.l.c. (SiO<sub>2</sub>; 20% acetone–chloroform); the original green band was gradually replaced with a more polar cherry red band. The mixture was poured into saturated sodium hydrogen carbonate solution and extracted with dichloromethane (3 × 100 ml), and the combined extracts were washed with aqueous sodium chloride (4 × 100 ml) and then water. The organic layer was evaporated to small volume (10 ml) and light petroleum added to precipitate the product, which was separated. Repetition of this procedure gave the *hydrochloride*, which crystallised from acetone–aqueous sodium chloride as purple needles (16.7 mg, 66%) (Found: Cl, 5.4; N, 8.6. C<sub>40</sub>H<sub>51</sub>ClN<sub>4</sub>O<sub>2</sub> requires Cl, 5.4; N, 8.6%), λ<sub>max</sub> 298, 396, 532, 563, and 608 nm (ε 12 780, 184 300, 9 410, 11 540, and 6 940), ν<sub>max</sub> 1 748 (C=O), 1 237, and 1 180 cm<sup>-1</sup> (C–O) (no NH band), τ (room temperature) -0.90 (s, 2 *meso*-H), -0.88 (s, 1 *meso*-H), -0.30 (s, 1 *meso*-H), 5.70 (16 H, m, 8 × CH<sub>2</sub>), 8.03 (24 H, m, 8 × CH<sub>3</sub>), 8.44 (2 H, q, ester CH<sub>2</sub>), 10.46 (3 H, t, ester CH<sub>3</sub>), and 15.64 (s, methine H; exchangeable with D<sub>2</sub>O) (no NH signal), τ (-55°) 11.85br (s, NH), *m/e* 618.3 (*M*–HCl, 100%) and 619.3 (*M*–Cl, 85.05%) by desorption method. In paper electrophoresis using 3% acetic acid the hydrochloride moved 1.1 cm in 30 min at 3 000 V and 24 mA, behaviour comparable with that of typical salts.

The chloride could be converted into the bromide and the perchlorate salts by repeatedly shaking a solution in dichloromethane with the appropriate sodium salt followed by isolation and crystallisation from acetone mixed with an aqueous solution of the sodium salt. The *perchlorate* was obtained as purple needles (Found: C, 67.0, H, 7.2; Cl, 5.0; N, 7.6. C<sub>40</sub>H<sub>51</sub>ClN<sub>4</sub>O<sub>8</sub> requires C, 66.8; H, 7.2; Cl, 4.9; N, 7.8%), λ<sub>max</sub> 395, 535, 568, and 618 nm (172 200, 8 960,

12 490, and 7 200),  $\nu_{\max}$  1 745 (C=O), 1 236, and 1 183  $\text{cm}^{-1}$  (C-O),  $\tau$  -0.89 (s, 2 *meso*-H), -0.73 (s, 1 *meso*-H), 0.30 (s, 1 *meso*-H), 5.70 (16 H, m, 8  $\times$  CH<sub>2</sub>), 8.03 (24 H, m, 8  $\times$  CH<sub>3</sub>), 8.44 (2 H, q, ester CH<sub>2</sub>), 10.22 (3 H, t, ester CH<sub>3</sub>), 11.90br (s, NH), and 15.70 (s, methine H; exchangeable with D<sub>2</sub>O), *m/e* 618 (*M*-HClO<sub>4</sub>, 80%).

(iii) The hydrochloride (above) (46.2 mg) was dissolved in dichloromethane (10 ml) and palladium(II) acetate was added. The mixture changed in colour from cherry red to greenish brown after several min and was stirred for 1 h. The product was poured into aqueous saturated sodium chloride (200 ml) and the porphyrins were extracted with dichloromethane (3  $\times$  100 ml). The extracts were washed with aqueous sodium chloride (2  $\times$  100 ml) and then water (100 ml), dried, and evaporated to 1 ml. The solution was chromatographed (preparative t.l.c.) on silica (50% acetone-light petroleum). The major band was separated and the *dichloropalladium* complex (IX) isolated; crystallisation from acetone-aqueous sodium chloride gave black needles (orange-green in solution) (28.3 mg, 48%) (Found: Cl, 8.7; N, 6.8. C<sub>40</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Pd requires Cl, 8.9; N, 7.0%),  $\lambda_{\max}$  320, 397, 443, 560, 584, and 630 nm ( $\epsilon$  18 280, 85 050, 32 570, 7 960, 10 310, and 4 700),  $\nu_{\max}$  1 745 (C=O), 1 226, and 1 189  $\text{cm}^{-1}$  (C-O), *m/e* 800 (8.63), 799 (8.91), 798 (11.42), 797 (6.12), 796 (16.99), 795 (8.63), and 794 (7.52%) (*M*<sup>+</sup> due to isotopes of palladium and chlorine), 620 (*M* + H<sub>2</sub> - PdCl<sub>2</sub>, 37.88%), and 619 (*M* + H - PdCl<sub>2</sub>, 100%) (field desorption method),  $\tau$  -0.60 (s, 2 *meso*-H), -0.24 (s, 1 *meso*-H), -0.11 (s, 1 *meso*-H), 5.74 (4 H, q, 2  $\times$  CH<sub>2</sub>), 6.09 (12 H, m, 6  $\times$  CH<sub>2</sub>), 8.14 (17 H, m, 5  $\times$  CH<sub>3</sub> and ester CH<sub>2</sub>), 8.49 (6 H, t, 2  $\times$  CH<sub>3</sub>), 8.74 (3 H, t, CH<sub>3</sub>), 10.61 (3 H, t, ester CH<sub>3</sub>), and 14.20 (sharp s, methine H; not exchangeable with D<sub>2</sub>O).

*Reaction of 21,22-Ethoxycarbonylmethyleneoctaethylporphyrin Hydrobromide with Sodium Hydroxide.*—The hydrobromide (44 mg) was shaken overnight with ethanolic sodium hydroxide (57 mg in 17 ml). The solution was poured into water and extracted with dichloromethane (3  $\times$  50 ml) and the extracts were washed and concentrated. Addition of methanol caused the separation of purple crystals of octaethylporphyrin (12.6 mg, 37.5%).

*21,22-Methyleneoctaethylporphyrin Hydriodide* (VIII; R = H).—Octaethylporphyrin (1 g) was suspended in redistilled methylene iodide (10 ml) containing anhydrous potassium carbonate (1.0 g). The degassed mixture was heated in a Carius tube in an atmosphere of nitrogen at 100 °C for 24 h. The solution was then diluted with chloroform (100 ml), filtered, and evaporated *in vacuo*. The residue was chromatographed on alumina (Spence type H); residual octaethylporphyrin (893 mg) was eluted with chloroform. Further elution with chloroform-methanol (9 : 1) gave a second band which was separated; the solution was washed with aqueous potassium iodide and then water, and evaporated. The

residue was crystallised from acetone-hexane and gave the *product* as purple microprisms (101 mg, 8%), m.p.  $\leq$  300 °C (Found: C, 65.5; H, 7.05; N, 8.45. C<sub>38</sub>H<sub>47</sub>IN<sub>4</sub> requires C, 65.95; H, 7.0; N, 8.3%),  $\lambda_{\max}$  397, 534, 564, and 612 nm ( $\epsilon$  98 400, 11 550, 13 800, and 8 900),  $\tau$  -0.35, -0.05, and 0.00 (4 *meso*-H, 1 : 2 : 1), 6.0 (16 H, 4 overlapping q of ethyl CH<sub>2</sub>), 8.1 (24 H, overlapping t of ethyl CH<sub>3</sub>), and 18.0br (s, bridging CH<sub>2</sub>).

*Reaction of 21,22-Methyleneoctaethylporphyrin Hydriodide with Potassium Iodide.*—The porphyrin salt (50 mg) was dissolved in acetone (50 ml) containing potassium iodide (200 mg) and the solution heated under reflux for 15 min. After addition of water (50 ml), the products were extracted with chloroform (2  $\times$  50 ml) and the extracts evaporated. Chromatography of the residue on alumina gave a single fraction, eluted with chloroform, which crystallised on evaporation and addition of methanol. The product was identified as 21-methyloctaethylporphyrin (36 mg, 89%) by comparison with an authentic specimen.<sup>11</sup>

*21,22-trans-Bis-(3-bromopropyl)octaethylporphyrin* (X; R = CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>Br).—Octaethylporphyrin (500 mg) was dissolved in 1,3-dibromopropane (25 ml) containing anhydrous potassium carbonate (1 g) and the mixture was heated under nitrogen at 100 °C for 240 h in a sealed tube. The solvent was removed and the residue chromatographed on alumina with benzene as eluant. The first brown band was separated and on purification yielded 21-(3-bromopropyl)octaethylporphyrin (282 mg, 46%).<sup>11</sup> A second band was obtained by elution with chloroform-methanol (9 : 1). The eluate was shaken with aqueous potassium bromide and then water and evaporated; the residue crystallised from acetone-hexane to yield purple needles of 21,22-trans-bis-(3-bromopropyl)octaethylporphyrin hydrobromide (313 mg, 39%) (Found: C, 58.4; H, 6.25; N, 6.3. C<sub>42</sub>H<sub>57</sub>Br<sub>3</sub>N<sub>4</sub> requires C, 58.8; H, 6.7; N, 6.55%),  $\lambda_{\max}$  405, 547, 578, and 626 nm ( $\epsilon$ , 147 400, 8 150, 12 200, and 5 400),  $\tau$  -1.08 (s, 1 *meso*-H), -0.3 (s, 3 *meso*-H), 5.9 (16 H, 4 overlapping q of ethyl CH<sub>2</sub>), 8.30 (6 H, t, 2 ethyl CH<sub>3</sub>), 8.60 (6 H, t, 2 ethyl CH<sub>3</sub>), and 11.9, 12.4, and 14.8 (all m, each 4 H, bromopropyl protons).

*Thermolysis of 21,22-trans-Bis-(3-bromopropyl)octaethylporphyrin Hydrobromide.*—The salt (10 mg) in redistilled *o*-dichlorobenzene (10 ml) was heated under reflux in nitrogen. After 2 h the solvent was removed *in vacuo* and the residue dissolved in chloroform and examined by chromatography; the sole product was octaethylporphyrin.

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