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ELECTROCHEMICAL CYANATION OF PORPHYRINS: MESO-MONO TO TETRACYANOOCTAETHYLPORPHYRINS

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Summary Electrochemical oxidation of Zn-octaethylporphyrin in the presence of CN^- gave meso-mono-, di-(ab+ac), tri- and tetracyanooctaethylporphyrin with good selectivity and yields.

The effect of electron-withdrawing substituents on the electrochemical behavior of porphyrins and metalloporphyrins is a way to measure the importance of metal-ligand and macrocycle-peripheral substituents interactions[3,4]. Cyano groups (directly attached to the macrocycle) are of particular interest since their sensitivity to steric factors is low and the created effects are large, as was demonstrated in the tetraphenylporphyrin (TPP) series[3]. Only monocyanation (CHO → CN or radical cation + CN^-)[5] of octaethylporphyrin (OEP), a better model for natural porphyrins, was known and polycyanation via bromination and substitution (CuCN), as for tetraphenylporphyrin[3], did not work. Therefore we used electrochemical methods[6] to achieve polysubstitution.

The reaction conditions were : substrate (1.25 to 2.5×10^{-3} M) dissolved in dimethylformamide + $Et_4N^+ClO_4^-$ (0.1 M) + $Et_4N^+CN^-$, platinum electrodes[7] (saturated calomel reference electrode).

Zinc-octaethylporphyrin (ZnOEP) was chosen as substrate for two reasons : a) better solubility in DMF as compared to H_2OEP, b) less positive oxidation potentials. Furthermore the first oxidation wave shifted to

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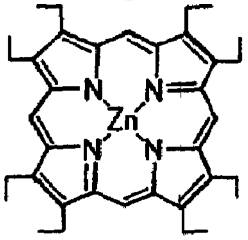

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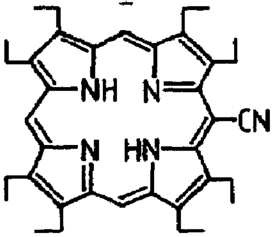

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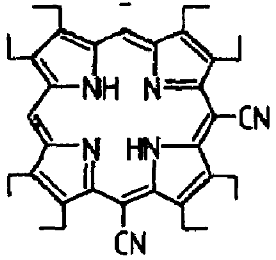

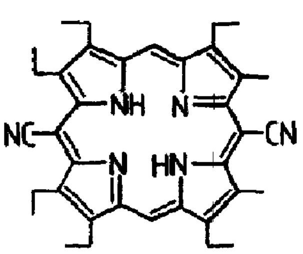

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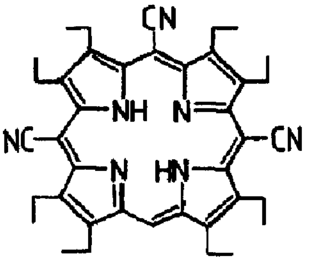

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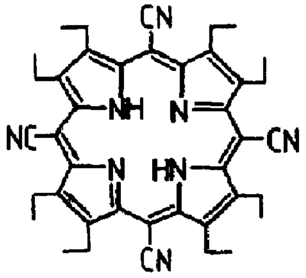

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even less positive values in the presence of CN^- owing to the equilibrium :

$$\underset{\underline{1}}{\text{ZnOEP}} \xrightleftharpoons{CN^-} \underset{\underline{A}}{[\text{Zn(CN)OEP}]^-}$$

ZnOEP was oxidized at $E_{1/2}$ = 730 mV / SCE (without cyanide) or $E_{1/2}$ = 500 mV / SCE (0.25 M $Et_4N^+CN^-$). The products (2 - 6) were isolated as free bases (HCl demetalation) and directly crystallized (2, 3 + 4) or chromatographed and crystallized (3 - 6).

Electrolysis of 1 at 450 mV ($Et_4N^+CN^-$ 0.25 M) gave quantitatively 2[8]. Similarly oxidation at 650 mV gave a ca 50:50 mixture of 3 and 4 (78 %) + some 5.

Oxidation to 5 and 6 proved to be less selective : in the 800-950 mV range (0.25 M $Et_4N^+CN^-$; higher potential were not used to avoid oxidation of CN^-) 6 was always the major isolated product (20-40 %) accompanied by 3, 4 and 5.

However on decreasing [$Et_4N^+CN^-$] from 0.25 M to 0.03 M 5 formed at the expense of 6 and was the major isolated product (30 %) at [$Et_4N^+CN^-$] = 0.03 M (+ traces of 6 and *ca* 20 % 3 + 4).

NMR ($CDCl_3$), δ ppm, 250 MHz :

	meso	CH_2 (quartets)	CH_3 (triplets)
H_2DEP	10.12	4.09	1.89
2	10.12(2H),10.02(1H)	4.02,4.04,4.07,4.32	1.88(12H),1.91(12H)
3	9.85	3.94,3.97,4.23,4.27	1.81(6H),1.84(12H),1.87(6H)
4	9.86	4.01(8H),4.23(8H)	1.84(12H),1.88(12H)
5	9.97	3.94,4.17,4.19,4.21	1.76,1.78,1.79,1.82
6	-	4.02	1.64

REFERENCES

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2) Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, E.R. associée au CNRS n° 468, Institut Le Bel, 4 rue Blaise Pascal, Strasbourg.

3) Cyano groups (and some other substituents) attached to pyrrolic carbons, see : H.J. Callot, *Bull. Soc. Chim. Fr.*, 1992 (1974) ; H.J. Callot, A. Giraudeau and M. Gross, *J. Chem. Soc. Perkin II*, 1321 (1975) ;

A. Giraudeau, H.J. Callot and M. Gross, *Inorg. Chem.*, 18, 201 (1979) ; A. Giraudeau, H.J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Amer. Chem. Soc.*, 101, 3857 (1979) ; R.F.X. Williams and P. Hambright, *Bioinorg. Chem.*, 9, 537 (1978) ; H.J. Shine, A.G. Padilla and S.M. Wu, *J. Org. Chem.*, 44, 4069 (1979).

4) Several studies involved phenyl substituted meso-tetraphenylporphyrins although the effect of the substituents was smaller. See for example: K.M. Kadish et al., *J. Amer. Chem. Soc.*, 99, 2381 (1977) ; *ibid.*, 98, 3326 and 8387 (1976) and related papers.

5) Cyano OEP via formylation : H.H. Inhoffen, J.H. Fuhrhop, H. Voigt and H. Brockmann Jr., *Liebigs Ann.*, 695, 133 (1966) ; A.W. Johnson and D. Oldfield, *J. Chem. Soc.* C, 794 (1966) ; via radical-cations : K.M. Smith, G.H. Barnett, B. Evans and Z. Martynenko, *J. Amer. Chem. Soc.*, 101, 5953 (1979) and references cited therein.

6) Electrochemical cyanation of aromatics is well documented : S.D. Ross, M. Finkelstein and E.J. Rudd, Anodic Oxidation, Acad. Press, New York, 1975, p. 94-96. Recent studies extended the reaction to various heterocyclic substrates : K. Yoshida, *J. Amer. Chem. Soc.*, 101, 2116 (1979) and earlier publications by the same author.

7) Under identical electrolysis conditions H_2TPP or ZnTPP only gave tars. We suppose that addition of CN^- on the corresponding radical-cation occurred also at the meso-position (cf. D. Dolphin, R.H. Felton, D.C. Borg and J. Fajer, *J. Amer. Chem. Soc.*, 92, 743 (1970)) but the resulting radical was rapidly overoxidized before tautomerisation to a β-substituted product could lead to stable β-cyanoporphyrins. However chemically generated ZnTPP radical-cation gives mono-β-substituted TPP's: see H.J. Shine, A.G. Padilla and S.M. Wu, *J. Org. Chem.*, 44, 4069 (1979).

8) Already described and identified with authentic sample (see ref. 5).

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