

Acid-catalysed Intramolecular Cobalt to Nitrogen Aryl Migration and Intramolecular Reverse Reaction in Cobalt Porphyrins. Synthesis of *N*-Phenylporphyrins

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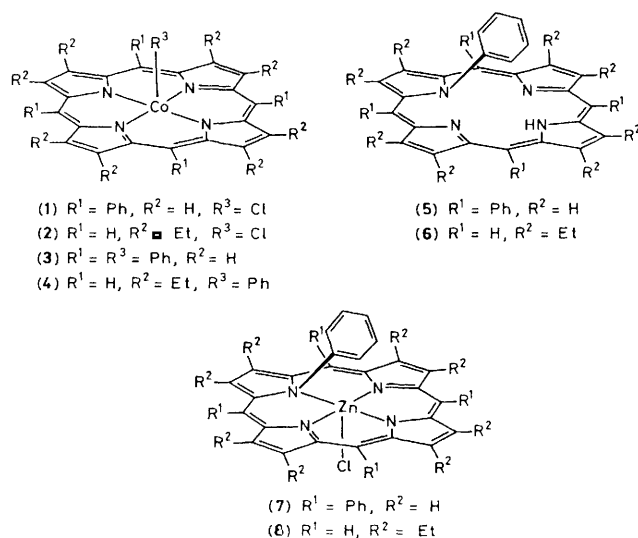
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On acid treatment phenylcobalt(III)porphyrins yielded *N*-phenylporphyrin bases, while the reverse reaction was performed upon metallation by cobalt(II) and reduction; double labelling experiments showed that both migrations are intramolecular.

We have recently reported¹ that α -styrylcobalt(III)porphyrins rearrange (and demetallate) to *N*- α -styrylporphyrins on acid treatment. Independently Dolphin² has described the reversible migration (Co \rightarrow N intramolecular; N \rightarrow Co intermolecular) of the ethyl group of ethylcobalt(III)tetraphenylporphyrin on electrochemical oxidation (Co \rightarrow N) and reduction (N \rightarrow Co). These results and the fact that a reverse migration of the α -styryl group can be efficiently induced by

a metallation–reduction sequence³ led us to reinvestigate both migrations.

Chlorocobalt(III)porphyrins (**1**) and (**2**) in benzene were treated with phenyl-lithium or phenylmagnesium bromide in ether⁴ to yield the corresponding phenylcobalt(III)porphyrins (**3**) and (**4**) (94 and 73%). Treatment of a 5×10^{-3} M solution of (**3**) and (**4**) in dichloromethane with trifluoroacetic acid (excess; 0.3 h), followed by neutralization (aqueous ammonia)



gave *N*-phenylporphyrins (5) and (6). These very basic products are better handled as chlorozinc complexes (7) or (8) [$\text{Zn}(\text{OAc})_2$ in methanol-chloroform followed by anion exchange; 76 and 70% yields respectively from (3) or (4); for ^1H n.m.r. data see Table 1].

N-Phenylprotoporphyrin was described as the product when haemoglobin (or haemin) was treated with phenylhydrazine.⁵ The above reaction sequence represents an easy access to this new series of *N*-substituted porphyrins, the identity of the substitution pattern being illustrated by the spectral properties (see Table 1).

Similar conditions also promote the migration of alkyl groups (Me, Et) from cobalt to a pyrrolic nitrogen atom. As a consequence of these observations our earlier interpretation for the α -styryl migration had to be dismissed since we now think that the fission of the Co-C bond is initiated by a decrease in electron density in the π system: electrogenerated cation radical,² or protons and oxygen (this work),[†] followed by migration of the intact group.

The mechanism of the reverse reaction had still to be clarified. Migration of an alkyl group from N to cobalt upon reduction of *N*-alkylated cobalt(II)porphyrins is well documented.^{2,6} Although an intermolecular S_N2 type reaction of cobalt(-I) has been postulated² on the basis of double labelling experiments, it is difficult to apply such a mechanism to α -styryl or phenyl migrations.

We prepared compounds $[\text{H}_5](3)$, $[\text{H}_{20}](3)$, and $[\text{H}_{25}](3)$ ($\text{Co}-\text{C}_6\text{D}_5$ from $\text{C}_6\text{D}_5\text{MgBr}$; $[\text{H}_{20}]\text{porphyrin}$ from $\text{C}_6\text{D}_5\text{CHO}$

Table 1. ^1H N.m.r. chemical shifts for chlorozinc-*N*-phenylporphyrins (*N*-phenyl group).^a

	δ		
	ortho	meta	para
(7)	2.38	5.17	5.66
(8)	ca. 2.0 ^b	4.92	5.46
Chlorozinc- <i>N</i> -phenylprotoporphyrin dimethyl ester ^c	2.02	4.95	5.50

^a δ from Me_4Si , CDCl_3 . ^b Masked by methyl resonances. ^c From reference 5.

[†] The observation, in vitamin B₁₂ coenzyme models, that the Co-C bond dissociation energy decreases with decreasing donating properties of a *trans* ligand may be related. See F. T. T. Ng, G. L. Rempel, and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 621.

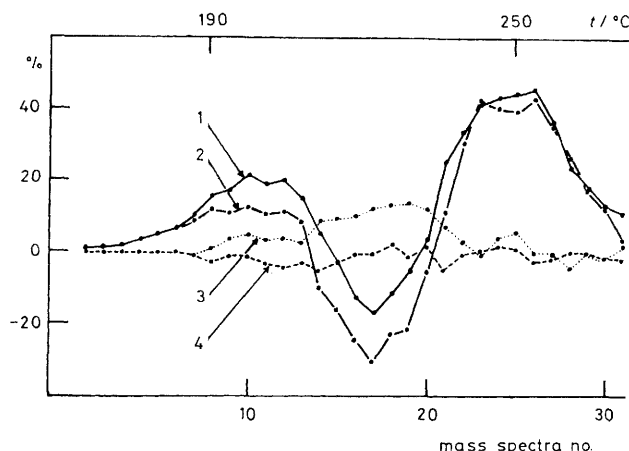


Figure 1. Mass spectral intensity difference curves for peaks corresponding to (3), $[\text{H}_5](3)$, $[\text{H}_{20}](3)$, and $[\text{H}_{25}](3)$ (crossed experiment starting with (5) and $[\text{H}_{25}](5)$; all measured curves adjusted to 0–100%). Curve 1: $\{(3) - [\text{H}_5](3)\}$, curve 2: $\{[\text{H}_{25}](3) - [\text{H}_{20}](3)\}$, curve 3: $\{(3) - [\text{H}_{25}](3)\}$, curve 4: $\{[\text{H}_5](3) - [\text{H}_{20}](3)\}$. Intensities for the (3) and $[\text{H}_{25}](3)$ peaks reached a maximum (100%) at spectrum no. 23, while the maximum for $[\text{H}_5](3)$ and $[\text{H}_{20}](3)$ was reached at spectrum no. 17.

and pyrrole). These and undeuterated (3) were subjected to the rearrangement conditions (concentration $5 \times 10^{-3} \text{ M}$) and gave (5), $[\text{H}_5](5)$, $[\text{H}_{20}](5)$, and $[\text{H}_{25}](5)$, respectively. A crossed experiment using (3) and $[\text{H}_{25}](3)$ demonstrated that no exchange occurred and confirmed the intramolecularity of the acid-catalysed migration. Metallation and reduction [cobalt(II) acetate, then sodium borohydride] gave the starting phenylcobalt(III)porphyrins (yield 83%). A crossed experiment using (5) and $[\text{H}_{25}](5)$ gave a product which showed 4 molecular peaks in the mass spectrum {corresponding to $[\text{H}_0]$, $[\text{H}_5]$, $[\text{H}_{20}]$, $[\text{H}_{25}](3)$; 15 eV, direct inlet}. However continuous recording of the intensities of these peaks over a temperature gradient (170–250 °C) demonstrated that: (a) peaks corresponding to (3) and $[\text{H}_{25}](3)$ behaved similarly; (b) peaks corresponding to $[\text{H}_5](3)$ and $[\text{H}_{20}](3)$ behaved similarly but very differently from the peaks of (3) and $[\text{H}_{25}](3)$ (they have a delayed appearance and a different position for the maximum intensity) (Figure 1). A blank experiment in which the same weight of (3) and $[\text{H}_{25}](3)$ were co-crystallized from dichloromethane-methanol and subjected to identical mass spectrometric conditions gave a very similar set of curves. We conclude that $[\text{H}_5](3)$ and $[\text{H}_{20}](3)$ are secondary products produced in the measurement of spectra, *via* Co-C bond fission and readdition, and that the reaction is intramolecular.

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References

- H. J. Callot and E. Schaeffer, *Tetrahedron Lett.*, 1980, 1335.
- D. Dolphin, D. J. Halko, and E. Johnson, *Inorg. Chem.*, 1981, **20**, 4348.
- H. J. Callot, unpublished results.
- D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc. C*, 1968, 881.
- P. L. Ortiz de Montellano and K. L. Kunze, *J. Am. Chem. Soc.*, 1981, **103**, 6534.
- H. Ogoshi, E. Watanabe, N. Koketzu, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1974, 943.