

Synthesis of Petroporphyrins with Six and Seven Membered Exocyclic Ring Systems

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Intramolecular cyclization of porphyrins substituted with either propanoic or butanoic acid side chains led to the formation of the cyclic ketones (**3c**) and (**4d**) from which the petroporphyrins (**3b**) and (**4c**) were obtained; treatment of (**4c**) under acidic conditions did not result in rearrangement of the seven membered exocyclic ring.

Examination of porphyrins occurring in petroleum and related deposits by modern chromatographic and spectroscopic procedures has revealed the presence of a wide range of interesting structural types. Apart from the ubiquitous deoxyphylloerythroaetioporphylin (DPEP) series (**1a—c**)^{†1—4} several other porphyrins have been recognised which contain five (**2**),⁵ six (**3a**) and (**3b**),⁶ and seven membered exocyclic rings (**4a—c**).^{7,8} Most of these structures are almost certainly derived from known chlorophylls. The DPEP series is clearly derived from chlorophyll *a* and the formation of the seven membered ring has been rationalised⁸ in terms of chemistry of this same chlorophyll established by Eschenmoser and his colleagues.⁹ It is suggested⁵ that compound (**2**) originates from an acid catalysed rearrangement of chlorophyll *c*.¹⁰ On the other hand the origin of the six membered system in (**3a**) and (**3b**) is not clear. It is possible that it is formed by intramolecular cyclization of a propanoic acid to yield a rhodin¹¹ followed by methylation and reduction; alternatively these compounds might be derived by rearrangement of the seven membered exocyclic ring system present in (**4b**) and (**4c**). In fact we thought it conceivable that porphyrins (**3a**) and (**3b**) were not naturally occurring petroporphyrins at all but were artefacts produced from (**4b**) or (**4c**) under the strongly acidic conditions used in their isolation, a procedure which included treatment with $\text{Ac}_2\text{O}/\text{SnCl}_4$ and hot MeSO_3H .⁶ Hence we have synthesised the petroporphyrins (**3b**) and (**4c**) with the aim of consolidating their structure and studying the possible conversion of (**4c**) into (**3b**) under acidic conditions.

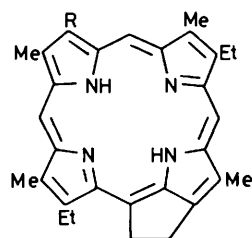
To this end the porphyrins (**5a**) and (**5b**) were prepared utilising the copper(II) chloride oxidative cyclization of appropriately substituted 1,19-dimethylbiladienes-*ac* in dimethylformamide at room temperature.¹² The biladienes were assembled in the 'clockwise' mode following chemistry developed by Smith and Craig.¹³ Cyclization of the acid chloride derived from (**5a**) with tin(IV) chloride in benzene gave the rhodin (**3c**) in 50% yield and the seven membered ketone (**4d**) was obtained in a similar manner and yield.

Reduction of (**4d**) with NaBH_3CN in the presence of ZnI_2 in refluxing 1,2-dichloroethane¹⁴ gave (**4c**) which as its nickel complex was shown to be identical by ^1H n.m.r. spectroscopy with the natural material. Reaction of the copper complex of (**3c**) in tetrahydrofuran with ethereal methyl-lithium between 0 and -10°C gave the tertiary alcohol which was not characterised but reduced with $\text{NaBH}_3\text{CN}/\text{ZnI}_2$ in 1,2-dichloroethane at room temperature to give (**3b**)[‡] after removal of the chelating metal by treatment with sulphuric acid in trifluoroacetic acid. The ^1H n.m.r. spectrum of this compound agreed well with published data.⁶

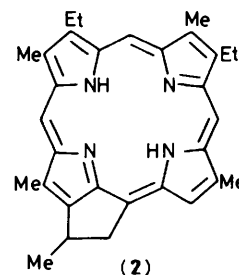
[†] These and subsequent petroporphyrins are represented for convenience as the free bases although they commonly occur naturally as nickel and/or vanadium complexes.

[‡] Recently a symmetrical porphyrin containing six membered exocyclic ring systems has been synthesised using tetrahydroindoles as intermediates.¹⁵

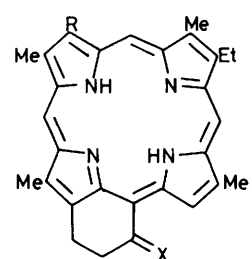
Treatment of the copper, nickel, or vanadyl complex of (**4c**) with methanesulphonic acid under nitrogen at 110–120°C for 2 h resulted in the removal of the metal and the isolation of the unaltered ligand shown to be identical with authentic material by ^1H n.m.r. spectroscopy and t.l.c. There was no evidence of the presence of the six membered exocyclic ring porphyrin (**3b**). Also when the nickel complex of (**4c**) was acylated with $\text{Ac}_2\text{O}/\text{SnCl}_4$ ^{6,16} and the product heated with methanesulphonic acid to remove the chelating metal and acetyl substituent, (**4c**) was again isolated without any evidence of



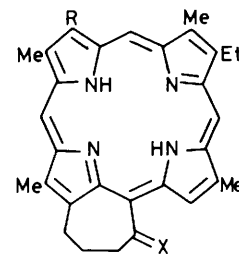
R
(1a) H
(1b) Me
(1c) Et



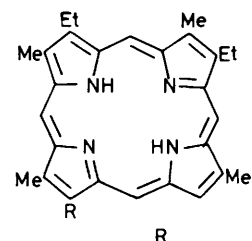
(2)



R X
(3a) Me Me, H
(3b) Et Me, H
(3c) Et O



R X
(4a) H 2H
(4b) Me 2H
(4c) Et 2H
(4d) Et O



R
(5a) $\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$
(5b) $\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$

the presence of rearranged material. These results support the view that the six membered exocyclic ring porphyrin (**3b**) is a genuine petroporphyrin and not an artefact of an isolation procedure although it leaves open the question of the origin of the methyl group in this six membered ring. There is the possibility of a secondary methylation, perhaps by bacterial action, although a rearrangement of (**4c**) to (**3b**) under geochemical conditions remains an option to be considered.

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