

TOTAL SYNTHESIS OF THE C₃₁ AND C₃₂ 15,17-BUTANOPORPHYRINS FROM OIL SHALES

Timothy D. Lash* and Marty C. Johnson

Department of Chemistry, Illinois State University, Normal, Illinois 61761, U.S.A.

Abstract: Copper(II) promoted cyclizations of a,c-biladienes incorporating seven-membered carbocyclic rings gave poor yields of porphyrins; however, superior yields of petroporphyrins 1a and 1b were obtained when cyclizations were mediated by silver iodate-zinc acetate.

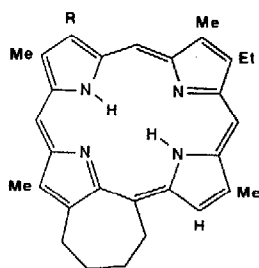
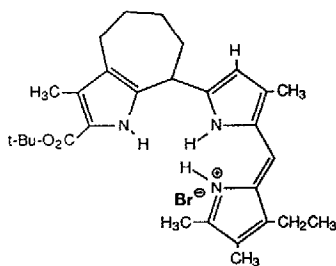
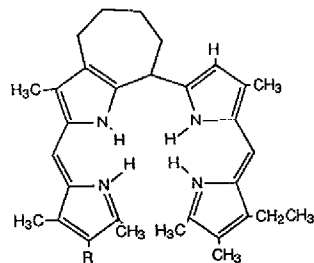
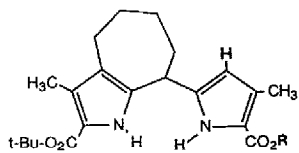
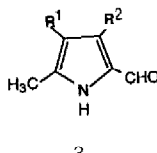
More than forty petroporphyrins¹⁻³ have been isolated and characterized from organic-rich sediments. In 1983, Maxwell and coworkers reported⁴ the isolation and characterization of a novel C₃₂ 15,17-butanoporphyrin 1a from Serpiano oil shale (Triassic, Switzerland). Later studies showed that a 3-methyl homolog 1b² and two possibly related methylpropanoporphyrins⁵ were also present. Fookes⁶ reported the characterization of three nickel 15,17-butanoporphyrins from the Julia Creek oil shale and the presence of 1a in Messel oil shale has also been noted³.

There is a need for synthetic samples of geochemically relevant porphyrins as chromatographic, spectroscopic and mass spectrometric standards. Recent studies in our laboratory⁷⁻⁹ have been directed towards the synthesis of petroporphyrins with exocyclic rings. We now report new syntheses of petroporphyrins 1a and 1b from b-cycloheptenopyrroles.

The novel pyrrolyl-b-cycloheptenopyrrole 2a was prepared in good overall yield by application of procedures similar to those described earlier^{7,9}. Hydrogenolysis of the benzyl ester over 10% palladium-charcoal gave the corresponding carboxylic acid 2b. Condensation of 2b with the pyrrole aldehyde 3a in the presence of p-toluenesulfonic acid, followed by brief treatment with dry HBr¹⁰, gave the tripyrrene hydrobromide 4 in 76% yield. Subsequent condensation of 4 with the 2-formylpyrrole 3b, in the presence of hydrobromic acid, gave the a,c-biladiene salt 5a in 90% yield.

Attempts to cyclize 5a in the presence of copper(II) chloride in dimethylformamide¹⁰ resulted, following demetallation, in the formation of only trace quantities (< 3%) of impure porphyrin. When the a,c-biladiene 5a was treated with copper(II) acetate in pyridine at 70°C, yields of 4-6% porphyrin were achieved. Clearly, the seven-membered exocyclic ring exerts a deleterious influence on porphyrin formation, presumably due to the geometry enforced on the tetrapyrrolic intermediate by the carbocyclic ring conformation.

Recently, Smith and Minnetian¹¹ investigated alternative reagents for a,c-biladiene cyclizations. They reported that silver iodate-zinc acetate mediated cyclizations of a,c-biladienes gave good yields of porphyrins under mild conditions. The a,c-biladiene 5a was found to react relatively slowly under these conditions but gave, after workup, the desired petroporphyrin 1a in a respectable 26% yield. Tripyrrene 4 was also used as an

1 a. R = Et; b. R = Me45 a. R = Et; b. R = Me2 a. R = CH₂Ph; b. R = H3

- a. R¹ = Me; R² = Et
 b. R¹ = Et; R² = Me
 c. R¹ = R² = Me

intermediate in the synthesis of the C₃₁ 15,17-butanoporphyrin 1b. Condensation of 4 with pyrrole aldehyde 3c in the presence of hydrobromic acid gave a,c-biladiene 5b in high yield. Cyclization with silver iodate-zinc acetate gave petroporphyrin 1b in 32% yield. These improved yields appear to be due to the increased stability of the cyclizing tetrapyrroles under the new reaction conditions.

Carbocyclic rings have a profound influence on porphyrin cyclizations but these effects are modified by a variety of additional factors⁸. Further studies are in progress to further clarify our understanding of these effects¹².

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1. R.H. Filby and G.J. Van Berkel in "Metal Complexes in Fossil Fuels", eds. R.H. Filby and J.F. Branthaver, ACS Symposium Series 344, ACS, Washington DC, 1987, pp2-39.
2. M.I. Chicarelli, S. Kaur and J.R. Maxwell, *ibid.*, pp40-67.
3. R. Ocampo, H.J. Callot and P. Albrecht, *ibid.*, pp 68-73.
4. G.A. Wolff, M. Murray, J.R. Maxwell, B.K. Hunter and J.K.M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1983, 922.
5. M.I. Chicarelli, G.A. Wolff, M. Murray and J.R. Maxwell, *Tetrahedron*, 1984, 40, 4033.
6. C.J.R. Fookes, *J. Chem. Soc., Chem. Commun.*, 1983, 1474.
7. T.D. Lash, K.A. Bladel and M.C. Johnson, *Tetrahedron Lett.*, 1987, 28, 1135.
8. T.D. Lash, *Tetrahedron Lett.*, 1988, 29, 6877.
9. T.D. Lash and T.J. Perun, Jr., *Tetrahedron Lett.*, 1987, 28, 6265.
10. J.A.P. Baptista de Almeida, G.W. Kenner, R. Rimmer and K.M. Smith, *Tetrahedron*, 1976, 32, 1793.
11. K.M. Smith and O.M. Minnetian, *J. Chem. Soc., Perkin Trans. I*, 1986, 277.
12. Very recently, an alternative synthesis of 1a, where the seven-membered exocyclic was introduced subsequent to porphyrin formation, has been reported: P.S. Clezy, C.J.R. Fookes and J.K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1988, 83.