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# FIRST SYNTHESIS OF (MESOPORPHYRINYL)-(2-PYRRYL)-METHANES

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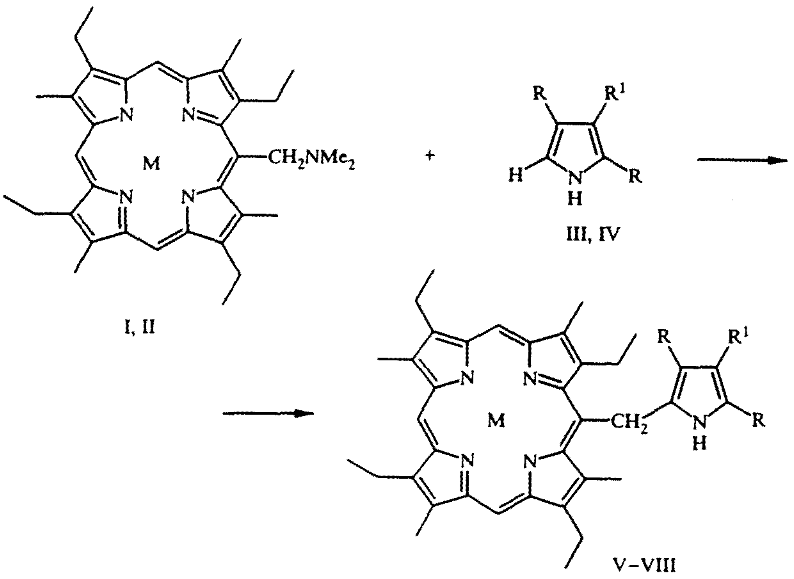
The possibility of generating mesoporphyrinylmethyl cations from readily available meso-N,N-dimethylaminomethylporphyrins, with the porphyrins either as the free bases or as metal complexes, has been demonstrated recently [1]. Several methods are available for the generation of mesoporphyrinylmethyl cations. For example, starting from the mesodimethylaminomethylporphyrin free base and an excess of zinc ethanoate, the zinc complex of the mesoporphyrinylmethanyl cation is produced which reacts with CH acids and alcohols to give zinc complexes of the corresponding alkylated products [2]. Another possible method to generate the mesoporphyrinylmethyl cation is decomposition of a trialkyl(mesoporphyrinylmethyl)-ammonium salt. Such compounds are readily obtained by treatment of the corresponding dimethylaminomethyl derivative with iodomethane at room temperature and the product can be detected by TLC or UV spectroscopy. Isolation of the quaternary salt was impossible because of its great lability. However, mesoalkoxymethylporphyrins were formed rapidly and readily on heating the quaternary ammonium salt with various alcohols in unstabilized chloroform solution [1]. It was also observed that dimeric ethanebisporphyrins were formed when quaternary ammonium salts were heated in unstabilized chloroform in the absence of a nucleophile [3].

Here we report a new reaction of mesomethyleneporphyrinyl cations with $\alpha$-unsubstituted pyrroles functioning as C$-$H acids.



I, V, VI M = 2H; II, VII, VIII M = Ni; III, V, VII R = R$^1$ = H; IV, VI, VIII R = CH$_3$, R$^1$ = COOC$_2$H$_5$

Reaction of meso-N,N-dimethylaminomethyl-etioporphyrin-1 (I) or its nickel complex (II) with pyrroles III and IV in unstabilized chloroform in the presence of excess iodoethane (with the free base I) or iodomethane (with the nickel complex (II)) gave a new type of compound, porphyrinylpyrrylmethanes in high yields (82-94%). Compounds V and VI required boiling for 4 h, while compounds VII and VIII were formed over 10 h at room temperature. Use of a 3- to 4-fold excess of pyrroles III and IV prevented the concurrent formation of the ethanebisporphyrins completely (see [3]).

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**Compound V.** $^1$H NMR spectrum (CDCl$_3$): 10.15 and 9.90 (two s, 2 H and 1 H, *meso*-H), 7.51 (br. s, 1 H, pyrrole-NH), 6.40 and 6.25 m, 5 H, PorC$\underline{H}_2$Pyr plus 3 × pyrrole-H), 4.20-3.95 (m, 8 H, PorC$\underline{H}_2$CH$_3$), 3.66, 3.65, 3.59 and 3.37 (s, 3 H, PorC$\underline{H}_3$), 1.88, 1.82 and 1.73 (all t, 3 H, 6 H and 3 H, *J* = 7.5 Hz, PorCH$_2$C$\underline{H}_3$), −2.80 ppm (br. s, 2 H, porphyrin-NH). UV spectrum (rel. intensity, chloroform): 408 (6.7), 504 (1.0), 540 (0.7), 572 (0.6), 624 nm (0.4). Mass spectrum, *m/z* (rel. intensity, %): 557 (M$^+$, 100), 492 (100).

**Compound VI.** $^1$H NMR spectrum (CDCl$_3$): 10.14 and 9.94 (two s, 2 H and 1 H, *meso*-H), 7.10 (br. s, 1 H, pyrrole-NH), 6.22 (m, 2 H, PorC$\underline{H}_2$Pyr), 4.30 (q 2 H, *J* = 7.5 Hz, OC$\underline{H}_2$CH$_3$), 4.10 (m, 8 H, PorC$\underline{H}_2$CH$_3$), 3.64, 3.63, 3.61, and 3.34 (s, 3 H, PorC$\underline{H}_3$), 2.70 and 1.90 (s, 3 H and 3 H, Me-pyrrole), 1.75, (m, 12 H, PorCH$_2$C$\underline{H}_3$), 1.36 (t, 3 H, *J* = 7.5 Hz, OCH$_2$C$\underline{H}_3$) −2.95 and −3.15 ppm (br. s, 1 H and 1 H, porphyrin-NH). UV spectrum (rel. intensity, chloroform): 406 (7.1), 504 (1.0), 540 (0.6), 575 (0.5), 624 nm (0.4). Mass spectrum, *m/z* (rel. intensity, %): 657 M$^+$, 100), 492 (6).

**Compound VII.** $^1$H NMR spectrum (CDCl$_3$): 9.45 and 9.44 (two s, 2 H and 1 H, *meso*-H), 6.55 (br. s, 1 H, pyrrole-NH), 6.05-5.90 (m, 5 H, PorC$\underline{H}_2$Pyr plus 3 × pyrrole-H), 3.95-3.75 (m, 8 H, PorC$\underline{H}_2$CH$_3$), 3.39, 3.38, 3.35 and 3.34 (s, 3 H, PorC$\underline{H}_3$), 1.76, 1.75, 1.70, and 1.67 ppm (all t, 3 H each, *J* = 7.5 Hz, PorCH$_2$C$\underline{H}_3$). UV spectrum (rel. intensity, chloroform): 406 (10.0), 530 (1.0), 564 nm (1.4). Mass spectrum, *m/z* (rel. intensity, %): 613 (M$^+$, 52), 548(2), 534 (100).

**Compound VIII.** $^1$H NMR spectrum (CDCl$_3$): 9.49 and 9.48 (two s, 2 H and 1 H, *meso*-H), 6.64 (br. s, 1 H, pyrrole-NH), 5.70 (br. s, 2 H, PorC$\underline{H}_2$Pyr), 4.30 (q, 2 H, OC$\underline{H}_2$CH$_3$) 3.95-3.65 (m, 8 H, PorC$\underline{H}_2$CH$_3$), 3.40, 3.41, 3.37 and 3.22 (all s, al 3 H, PorC$\underline{H}_3$), 2.56 and 1.93 (two s, 3 H and 3 H, Me-pyrrole), 1.78, 1.70, and 1.63 (all t, 3 H, 6 H and 3 H, *J* = 7.5 Hz, PorCH$_2$C$\underline{H}_3$), 1.38 ppm (t, 3 H, *J* = 7.5 Hz, OCH$_2$C$\underline{H}_3$). UV spectrum (rel. intensity, chloroform): 404 (10.0), 524 (1.0), 560 nm (1.0). Mass spectrum, *m/z* (rel. intensity, %): 713 (M$^+$, 100), 548(26).

The chemical properties of these unexpected porphyrin derivatives, with the pyrrole residue attached to the methylene bridge, are being studied at present. The most interesting prospect is the conversion of these compounds into porphyrinylpyrrolylmethenes (similar to the conversion of dipyrrolylmethanes into dipyrrolylmethenes) and the creation of a new type of conjugated system.

## REFERENCES

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