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SYNTHESES OF 5-ARYL- AND 5,15-DIARYL-2,3,7,8,12,13,17,18-OCTAETHYLPORPHINES

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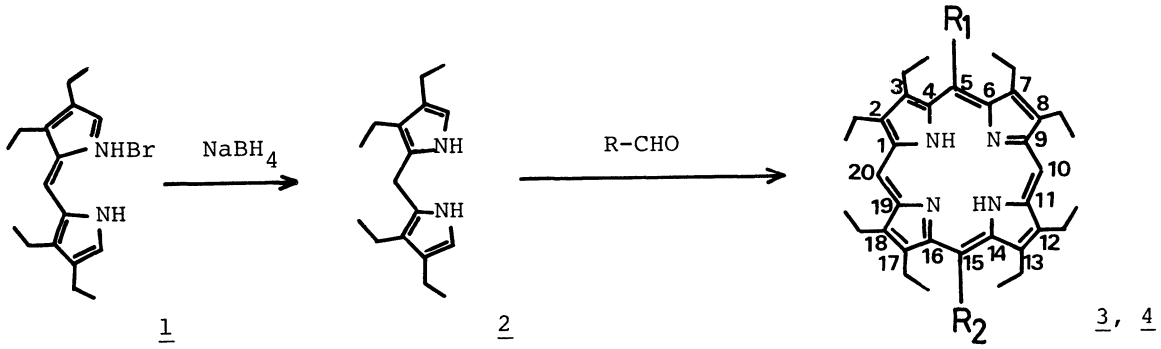
5-Aryl- and 5,15-diaryl-2,3,7,8,12,13,17,18-octaethylporphines were prepared with high selectivity by the condensation of bis-(3,4-diethylpyrryl)methane with aromatic aldehydes by varying acidic media.

The latest progress in the syntheses of porphyrins has led to give a deep insight into the function of hemoproteins. The meso-tetraarylporphines have been readily available for model ligands of hemoproteins. Recently Smith and his coworkers have reported the synthesis of sterically crowded meso-tetraphenyloctaethylporphine by the condensation of 3,4-diethylpyrrole with benzaldehyde.[1] Introduction of alkyl groups at the β-positions of pyrrole seems to hinder the free rotation of the meso-aryl group due to steric constraint. Baldwin and his coworkers have obtained a 5,15-diaryloctamethylporphine linked by a long bridge at the 2-positions of two phenyl groups.[2] The strapped porphyrins substituted with aryl groups at 5 and 15 positions were prepared from the 2-(substituted phenyl)dipyrrylmethane. In this letter we report facile and selective syntheses of 5-aryl(meso-monoaryl)- and 5,15-diaryl(meso-α,γ-diaryl)-2,3,7,8,12,13,17,-18-octaethylporphines involving large substituent such as 1-naphthyl group.

Reduction of 3,3',4,4'-tetraethyldipyrromethene hydrobromide 1 with $NaBH_4$ in ethanol afforded bis(3,4-diethylpyrryl)methane 2 quantitatively. A mixture of 2, aromatic aldehyde, and zinc acetate in propionic acid was refluxed for 3 hr. The 5-aryloctaethylporphines(3a,3b,3c,3d,3e,3f,3g and 3h) were isolated by using preparative thin layer chromatography in 15-25 % yields. On the other hand, the condensation of 2 with aromatic aldehydes in benzene including catalytic amount of

trifluoroacetic acid followed by aeration on alumina gel gave 5,15-diaryl-2,3,7,-8,12,13,17,18-octaethylporphines (4a,4b,4c,4d,4e,4f,4g and 4h) in 30-40 % yields exclusively. Trace amounts of monoarylporphyrin were detected by thin layer chromatography. The condensation of dipyrromethene hydrobromide 1 with aromatic aldehydes gave no meso-substituted octaethylporphines due to low reactivity of the α-carbon of the pyrrole towards electrophiles.[3] Formation of 5-aryloctaethylporphine 3 seems to result from the elimination of the aryl group during the oxidative aromatization from the phlorin to the porphine.



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	R1	R2		R1	R2
3a	Ph	H	4a	Ph	Ph
3b	2-MeOPh	H	4b	2-MeOPh	2-MeOPh
3c	3-MeOPh	H	4c	3-MeOPh	3-MeOPh
3d	4-MeOPh	H	4d	4-MeOPh	4-MeOPh
3e	2-MePh	H	4e	2-MePh	2-MePh
3f	3-MePh	H	4f	3-MePh	3-MePh
3g	4-MePh	H	4g	4-MePh	4-MePh
3h	1-naphthyl	H	4h	1-naphthyl	1-naphthyl

The 5,15-diaryloctaethylporphines 4b,4c,4e,4f and 4h derived from 2- or 3-substituted benzaldehydes and 1-naphthaldehyde may include two geometric isomers. Each of the two substituents at 2- or 3-position of aryl groups is above and below the porphyrin plane in the trans form (C_{2v} symmetry), whereas the two substituents are on the same side of the plane in the cis form (C_{2h} symmetry). However, two isomers could not be distinguished by the 100 MHz ^{1}H-nmr spectra of these porphyrins.

In the nmr spectrum the proton signals of the methylene group of the ethyl groups adjacent to the meso-aryl group appear at a higher magnetic field by about 1.5 ppm than those of octaethylporphine due to the diamagnetic ring current of the

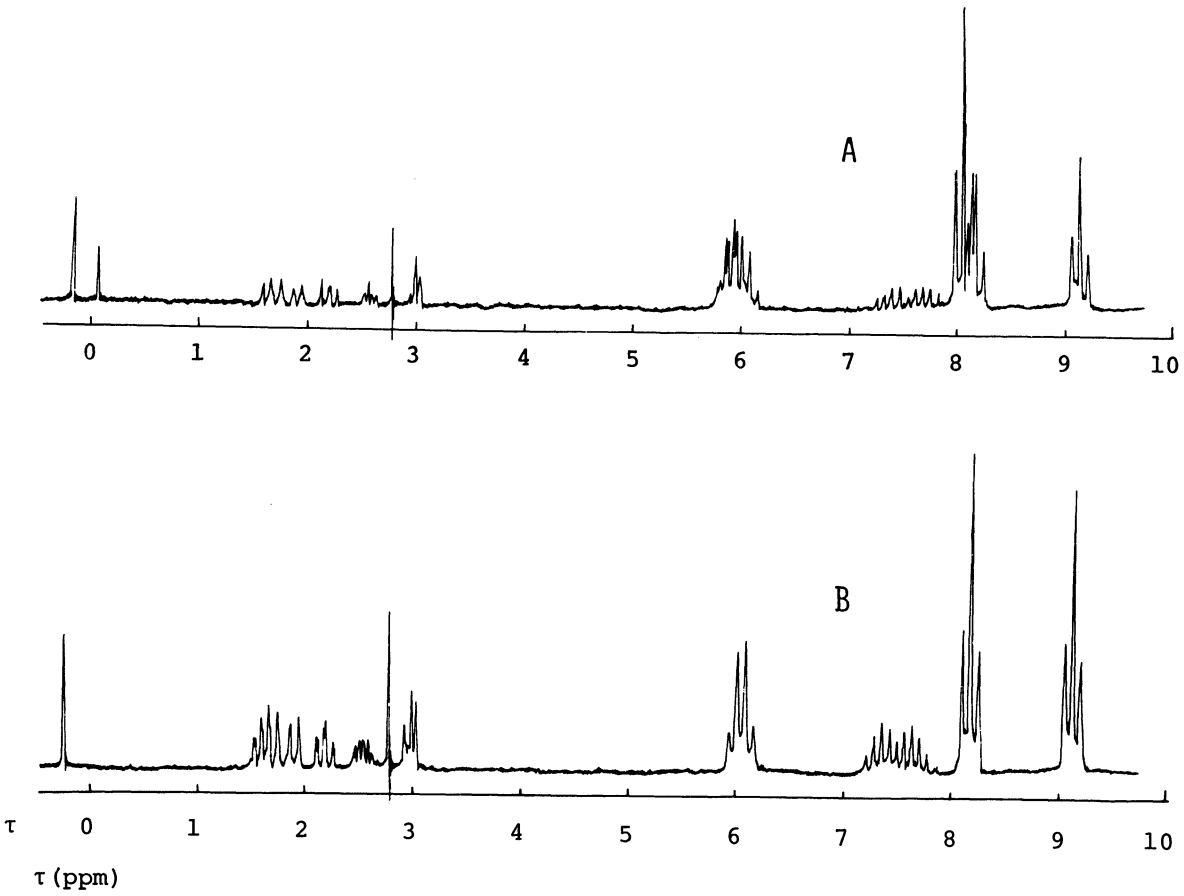

Fig. 1 100 MHz ^{1}H-nmr spectra of (A) 5-(1-naphthyl)-octaethylporphine (3h) and (B) 5,15-di-(1-naphthyl)-octaethylporphine (4h) in $CDCl_3$.

meso substituted aryl group. This fact indicates the presence of strong steric constraint in the proximity of the meso position. In particular the ethyl protons adjacent to the 2- or 3-substituted aryl and 1-naphthyl groups split into the ABX_3 pattern, whereas those for the 4-substituted aryl groups split into the normal A_2X_3 pattern as is shown in Fig. 1.

Table 1 lists the visible spectra of the 5-aryloctaethylporphines and 5,15-diaryloctaethylporphines. Introduction of the aryl group to the meso position of octaethylporphine results in the red shift of the absorption maxima and increase of the absorption strength of the β-bands involving vibronic exitation ($0 \longrightarrow 1$).[4] Microanalyses and spectral properties of these compounds show good agreement with the proposed structures. Isolation and structure determination of 5,15-di(2- or 3-substituted phenyl)octaethylporphines and 5,15-di(1-naphthyl)octaethylporphine

are in progress.

Table 1. Electronic spectra of 5-aryl-octaethylporphines and 5,15-di(4-substituted phenyl)octaethylporphines in $CHCl_3$

Compound	λ_{max}(nm) ($\log\varepsilon_{max}$)				
3a	407(5.91),	505(3.93),	539(3.68),	573(3.61),	626(3.29)
3b	407(5.22),	505(3.93),	539(3.65),	573(3.63),	627(3.19)
3c	407(5.26),	505(3.94),	539(3.69),	573(3.68),	626(3.28)
3d	407(5.28),	505(4.03),	539(3.75),	573(3.71),	626(3.19)
3e	407(5.27),	505(3.94),	539(3.64),	573(3.61),	626(3.28)
3f	407(5.27),	505(3.93),	539(3.69),	573(3.68),	626(3.19)
3g	407(5.25),	505(3.91),	539(3.65),	573(3.71),	626(3.20)
3h	407(5.19),	505(3.63),	540(2.43),	573(3.43),	627(3.18)
4a	413(5.23),	511(3.96),	544(3.46),	578(3.71),	630(2.89)
4d	414(5.31),	511(4.09),	544(3.72),	578(3.82),	631(3.42)

References and Notes

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