

## VI Summary

The aim of this work was the development of synthetic methods for the generation of unsymmetrical porphyrins with substituents exclusively at the *meso*-positions. Two points were of importance:

- synthesis of A- and *cis*-A<sub>2</sub>-porphyrins with functional groups in one and/or two neighboring *meso*-positions.
- the introduction of protected formyl groups of the *meso*-positions to allow later introduction of functional groups in an unsymmetrical manner.

The synthesis of porphin in larger quantities, gave a good basis for the successive development of substituted porphyrins. The modification of porphin with different organolithium compounds (butyl-, hexyl-, phenyllithium and 2-methoxyphenyllithium) allowed an easy entrance to so far inaccessible mono-substituted porphyrins. The 5,10-disubstituted porphyrins were similarly obtained by a modification of this method. Only few examples were known and their synthesis always involved extensive total syntheses. Use of reagents without sterical hindrance such as butyl- and hexyllithium supplied disubstituted porphyrins in very good yields between 60 and 90%. Employment of phenyl lithium gave yields of 43%. Monosubstituted porphyrins were obtained in yields up to 48%.

A second synthetic method for 5,10-A<sub>2</sub>-porphyrins was developed on the basis of a [3+1]-condensation. The synthesis of alkyl and aryl porphyrins in yields of 4 bis 11 % was possible via this route and monosubstituted porphyrins were received as by-products during this synthesis. The lower yields of this method were more than compensated by its simple procedure.

Within the framework of these investigations, it could be shown that the generation of unsymmetrical porphyrins is possible with more than 2 *meso*-substituents starting from 5,15-AB-porphyrins. The introduction of further groups of the free *meso*-positions occurred easily with organolithium reagents in different yields, ranging from 40 % to 90 %, and porphyrins of the ABC- and ABCD-type could be synthesized. Its manganese(III)complexes were utilized for initial studies on their suitability for styrene epoxidations. A porphyrin with bridging substituents was prepared and its manganese(III)complex was examined for its catalytic suitability.

The introduction of protected formyl groups succeeded by use of the 1,3-dithiane-2-yl group. Porphyrins containing both, 1,3-dithiane-2-yl- and phenyl substituents like 5,15-bis(1,3-dithiane-2-yl)-10,20-diphenylporphyrin and 5-(1,3-dithiane-2-yl)-10,15,20-triphenylporphyrin were prepared by various mixed [2+2]-condensations. 5-(1,3-dithiane-2-yl)dipyrromethane, a key precursor of these syntheses was obtained by reaction of 2-formyl 1,3-dithiane with pyrrole in 99 % yield. Porphyrins with exclusively 1,3-dithiane-2-yl groups were produced by a [2+2]-condensation or by a direct condensation of the aldehydes with pyrrole in the presence of acid, and gave an entry into 5,15-bis-, 5,10,15-tris- and 5,10,15,20-tetrakis(1,3-dithiane-2-yl)porphyrins. 5,10-bis(1,3-dithiane-2-yl)porphyrin was prepared by using a [3+1]-condensation method.

Initial experiments on the dethioacetalisation of the protected formyl groups were performed. In order to split off this group, DDQ in the presence of acid was used and gave good results for some compounds. E.g. 5,15-diformyl-10,20-diphenylporphyrin and 5-formyl-10,15,20-triphenylporphyrin could be prepared in yields of 96 % and 97 %. The elimination of the protective group from solely 1,3-dithiane-2-yl-substituted porphyrins was more difficult. Reaction of 5,15-bis-(1,3-dithiane-2-yl)porphyrin with bis(trifluoroacetoxy)iodobenzene led to the formation of 5(dimethoxymethyl)-15-formylporphyrin, while 5-formylporphyrin was obtained in 60 % yield. Tests on the dethioacetalisation of 5,10,15-tris- and 5,10,15,20-tetrakis(1,3-dithiane-2-yl)porphyrin so far resulted in the formation of mixtures of partially deprotected compounds.