Synthetic Studies Towards Novel Annulated Porphyrins

A Thesis Submitted Towards the Degree of

Doctor of Philosophy

by

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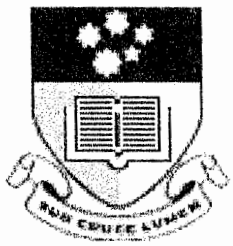

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Abstract

The synthesis of annulated porphyrins by the condensation of annulated monopyrroles and dipyrromethanes under a variety of conditions was investigated, with the aim to prepare model porphyrins for the investigation of conformational exchange of non-planar porphyrins in solution.

Cyclic alkenes incorporating oxygen, sulfur, silicon and nitrogen atoms were prepared as the primary starting materials for this study. Cyclopentene derivatives were also prepared. Carbon, oxygen, sulfone and nitrogen based cyclic vinyl sulfones were prepared by addition of benzenesulfenyl chloride, oxidation of the intermediate α-chlorosulfide, followed by elimination of HCl or alternatively by the addition of iodine and *p*-toluene sulfinate followed by elimination of HI. A silicon based cyclic vinyl sulfone could not be prepared due to the preference of the precursor molecules to give cyclic siloxanes or siloxane dimers during functionalisation to vinyl sulfones. Vinyl sulfones were also prepared directly by the condensation of malononitrile or dimethyl malonate with 2,3-bis(phenylsulfonyl)-1,3-butadiene.

A total of sixteen annulated[3,4-*c*]pyrrole 2-carboxylates were formed using a modified Barton and Zard condensation of vinyl sulfones and an isocyanoacetate anion. The conditions for this procedure were shown to be general for the formation of annulated pyrroles. Annulated dipyrromethanes were prepared from the corresponding pyrrole 2-carboxylates.

Only one porphyrin was prepared, namely $2^2,2^2,7^2,7^2,12^2,12^2,17^2,17^2$-octamethyl-2,3,7,8,12,13,17,17,18-cyclopentaporphyrin which was synthesised in 6-10% yield by acid catalysed condensation of 5,5-dimethyl-tetrahydrocyclopenta[*c*]pyrrole with formaldehyde or acid catalysed condensation of 2-hydroxymethyl-5,5-dimethyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrole. Black polymeric material was the only product isolated from attempts to form heteroannulated porphyrins by condensation of annulated monopyrroles or annulated dipyrromethanes.