Synthetic Studies Towards Novel Annulated Porphyrins

A Thesis Submitted Towards the Degree of
Doctor of Philosophy

by

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Abstract

The synthesis of annulated porphyrins by the condensation of annulated monopyroles and dipyromethanes 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, sulfur and nitrogen based cyclic vinyl sulfones were prepared by addition of benzene-sulfonyl chloride, oxidation of the intermediate α-chlorosulfide, followed by elimination of HCl or alternatively by the addition of iodine and p-toluene sulfonate 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-benadione.

A total of sixteen annulated 2,4-cyclopyrole 2-carboxylates were formed using a modified Barton and Zard condensation of vinyl sulfones and an isocyanate/acrylonitrile. The conditions for this procedure were shown to be general for the formation of annulated pyroles. Annulated dipyromethanes were prepared from the corresponding pyrole 2-carboxylates.

Only one porphyrin was prepared, namely 22,25,27,29,122,172,177-octamethyl-2,3,7,8,12,13,17,18-cyclopentakorophyrin which was synthesised in 6-10% yield by acid catalysed condensation of 5,5-dimethyl tetrahydrocyclopenta[ε]pyrole with formaldehyde or acid catalysed condensation of 2-hydroxymethyl-5,5-dimethyl-2,4,5,6-tetrahydrocyclopenta[ε]pyrole. Black polymeric material was the only product isolated from attempts to form heteroannulated porphyrins by condensation of annulated monopyroles or annulated dipyromethanes.