

Synthetic Approaches to Porphyrins by (2 + 2) Routes



Biography

Zhang Zongyao was born in Shandong province, China. He enrolled at Renmin University studying chemistry and obtained his B.Sc. degree in 2015. He then joined Prof. Cao Rui's group at Renmin University as a graduate student majoring in organic chemistry. His research interests include the development of porphyrin-based water oxidation electrocatalysts, molecular ion-exchange materials, and flexible coordination cages.

Institution

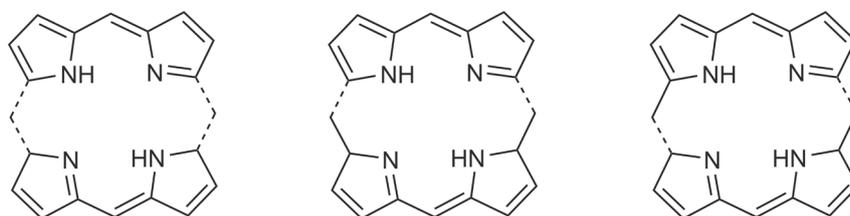
Renmin University of China

Abstract

In this case study, synthetic approaches toward porphyrins were investigated using *Science of Synthesis* Online. The search provided us with common synthetic pathways as well as credible remarks. The various bond-forming strategies presented were of great help.

Discussion

Our group is currently interested in investigating mononuclear compounds based on porphyrin for use as water oxidation electrocatalysts. Not being organic synthetic chemists, initially, reliable synthetic approaches using well-defined synthesis plans and easily handled experimental conditions needed to be researched and evaluated. Also, methods providing easy routes to simultaneously introduce functionality into the porphyrins were preferred. In this way, structure and full text searches were applied. A directly relevant section, on porphyrins and related compounds (Section 17.8) was found. Under this title, subsections depicted methods as one-pot synthesis from monopyrrole tetramerization, two-step (2 + 2) synthesis from dipyrromethenes, dipyrromethanes, or dipyrroketones as intermediates, two-step (3 + 1) synthesis from tripyrrole intermediates, and ring-closing reactions from open-chain tetrapyrrole intermediates.

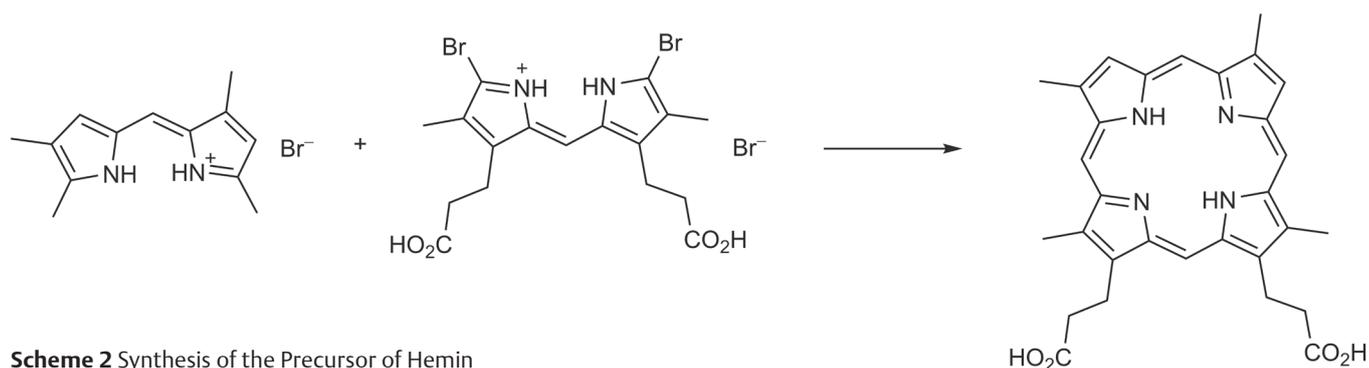


Scheme 1 Synthetic Approaches to Porphyrins by (2 + 2) Routes

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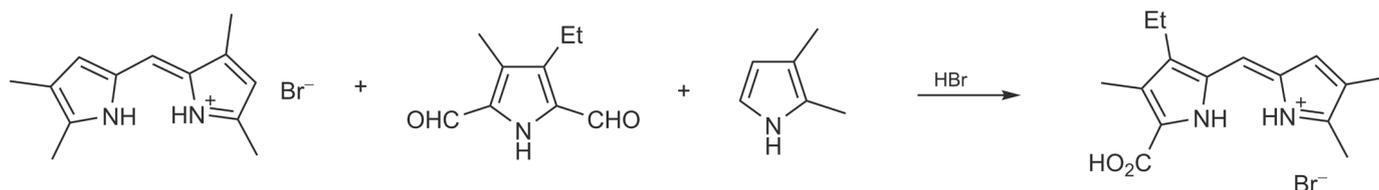
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Taking (2 + 2) routes from dipyrrolic Intermediates as an example, in Section 17.8.1.2.2.1, a synthesis requiring boiling dipyrromethenes in formic acid or in organic acid melts at high temperatures ($\leq 200^\circ\text{C}$) was described. A practical example was given, showing the synthesis of hemin by a (2 + 2) route from substituted dipyrromethenes.



Scheme 2 Synthesis of the Precursor of Hemin

We also searched for the synthesis of dipyrromethenes using structure search, which led us to Section 17.8.1.1.1.1 and other chapters such as Section 17.3.4.3.3.1.1.1.1, where dipyrromethenes are used to prepare interesting chromophoric compounds. In the section on dipyrromethenes (Section 17.8.1.1.1.1) the condensation of a 2-formyl-1*H*-pyrrole with a 2-unsubstituted 1*H*-pyrrole in the presence of acid was depicted. An example followed, giving exact experimental conditions. The remark that dipyrromethenes tend to spread widely on columns, was of great help.



Scheme 3 Synthesis of a Typical Dipyrromethene

Conclusion

Science of Synthesis Online is a powerful tool for organic chemistry researchers, which can be handled conveniently. It is of particular value for researchers from other fields, since *Science of Synthesis* Online provides them with validated synthetic routines with detailed experimental conditions and procedures. Furthermore, complementary reviews make it a peer-reviewed credible encyclopedia.