1,3-Dipolar Cycloaddition Reactions of *meso*-Tetra(2'-thienyl)porphyrins with a Nitrile Oxide

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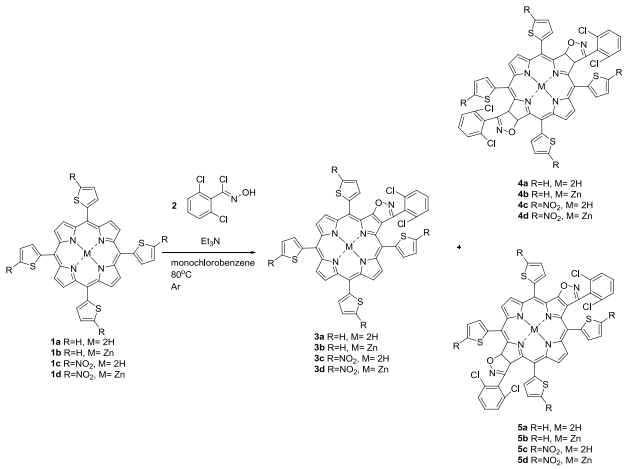
INTRODUCTION

Tetrathienylporphyrins have gained much interest recently due to their remarkable photophysical and electrochemical properties.[1] Derivatives such as chlorins, isobacteriochlorins and bacteriochlorins, can be synthesized by reduction with diimide or *para*-toluenesulfonylhydrazide, as well as oxidation with OsO_4, and Diels-Alder reactions and 1,3-dipolar cycloadditions, on the peripheral double bonds of the pyrrolic rings.[2,3] Chlorins and bacteriochlorins have been used in several scientific areas, especially in medicine. We have now explored the 1,3-dipolar cycloaddition of 2,6-dichlorobenzonitrile oxide with tetra(2'-thienyl)porphyrins **1a-d** (Scheme 1). We observed that tetra(2'-thienyl)porphyrins can react with the dipolarophile yielding chlorins and bacteriochlorins. These new compounds are candidates for use in photodynamic therapy (PDT) and solar cells studies.

RESULTS AND DISCUSSION

The 1,3-dipolar cycloaddition reactions of 2,6-dichlorobenzonitrile oxide with tetra(2'-thienyl)porphyrins and metallo-tetra(2'-thienyl)porphyrins **1a-d** yielded isoxazole-fused chlorins and bacteriochlorins (Scheme 1 and Table 1). The reactions were conducted with an excess of 2,6-dichlorobenzonitrile oxide at 80°C under argon atmosphere for 24-48 h, giving complex mixtures containing chlorins as the major product (Table 1), except for porphyrin **1c** which gave chlorins and bacteriochlorins in similar yields of 13-15%. After work-up and purification, the structures of the new compounds were confirmed by ^{1}H NMR, ^{13}C NMR, HRMS and UV/Vis spectroscopies.

We are now performing studies on aggregation in solution, singlet oxygen generation and photobleaching in order to select some compounds for PDT studies.



Scheme 1. Reaction of porphyrins **1a-d** with 2,6-dichlorobenzonitrile oxide.

Table 1. Product yields of porphyrins **1a-d** with 2.6-dichlorobenzonitrile oxide.

Entry	Time (h)	**3** (% yield)	**4** (% yield)	**5** (% yield)
1	24	(a) 13	(a) traces	(a) traces
2	24	(c) 15	(c) 13-	(c) 14
3	48	(b) 9	(b) traces	(b) traces
4	48	(d) 22	(d) traces	(d) traces

CONCLUSION

meso-Tetra(2'thienyl)porphyins **1a-d** participate in 1,3-dipolar cycloaddition reactions yielding new thienylchlorins and thienylbacteriochlorins.

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