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

Patrícia B. Momo, Ricardo B. Ayres, Timothy J. Brocksom, Kleber T. de Oliveira*

Universidade Federal de São Carlos - UFSCar, Departamento de Química, 13565-905, São Carlos, SP, Brazil.

*e-mail: kleber.oliveira@ufscar.br; www.lqbo.ufscar.br

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INTRODUCTION

Tetrathienylporphyrins have gained much interest recently due to their remarkable photophysical and electrochemical properties. Derivatives such as chlorins, isobacteriochlorins and bacteriochlorins, can be synthesized by reduction with diimide or para-toluenesulfonylhydrazide, as well as oxidation with OsO₄ and Diels-Alder reactions and 1,3-dipolar cycloadditions, on the peripheral double bonds of the pyrrolic rings. 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 (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 ¹H NMR, ¹³C 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>3 (% yield)</th>
<th>4 (% yield)</th>
<th>5 (% yield)</th>
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<tr>
<td>1</td>
<td>24</td>
<td>(a) 13</td>
<td>(a) traces</td>
<td>(a) traces</td>
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<tr>
<td>2</td>
<td>24</td>
<td>(c) 15</td>
<td>(c) 13-15</td>
<td>(c) 14</td>
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<td>3</td>
<td>48</td>
<td>(b) 9</td>
<td>(b) traces</td>
<td>(b) traces</td>
</tr>
<tr>
<td>4</td>
<td>48</td>
<td>(d) 22</td>
<td>(d) traces</td>
<td>(d) traces</td>
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</table>

CONCLUSION

meso-Tetra(2’thienyl)porphyrins 1a-d participate in 1,3-dipolar cycloaddition reactions yielding new thienylchlorins and thiencylbacteriochlorins.

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REFERENCES