Oxygenation of phenanthriporphyrin and copper(III) phenanthriporphyrin : an efficient route to phenanthribilinones.

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Streszczenie

Photooxidation of copper(III) 5,6-dimethoxyphenathriporphyrin and copper(III) 5,6-dioxophenanthriporphyrin, which contain phenanthrene or dioxophenathrene moieties built into the macrocyclic frameworks, resulted in the regioselective cleavage that afforded organometallic copper(III) complexes of open-chain phenanthribilinone-type acyclic ligands terminated by carbonyl groups. The copper(III) coordinates two carbon atoms of phenantherene (dioxophenanthrene) and two nitrogen atoms of pyrrole and pyrrolone units, preserving the donor sets of the paternal complexes. The primary dioxygen attack is located at the *meso* carbon atom adjacent to the phenanthrene moiety. Demetalation of copper(III) 21-benzoyl-phenanthribilin-1-one and copper(III) 21-benzoyl-dioxophenanthribilin-1-one yielded mainly two diastereomers [**15*Z***, **20*E***] and [**15*Z***, **20*Z***], which differ in the configurations at two C_{α}–C_{meso} double bonds. The regioselectivity of the cleavage, detected in the course of experimental studies, has been substantiated by DFT investigations. The regioselective cleavage of 5,6-dimethoxyphenanthriporphyrin in reaction with basic iron(III) acetate was detected, providing the synthetically efficient methodology to produce 21-benzoyl-dioxophenanthribilin-1-one.

Adres publiczny

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https://www.acs.org/content/acs/en.html