Chemical and photo generation of high-valent manganese-oxo porphyrins

Catalytic oxidations are some of the most important transformation reactions in the petrochemical and pharmaceutical industries. The drive for greener industrial processes has encouraged the use of biomimetic molecules for synthetic processes. Metalloporphyrins, inspired by the active site of cytochrome P450, have long been valued for their ability to perform catalytic oxidations with high regio- and stereospecificity. Three porphyrin systems possessing electron-withdrawing substituents were investigated for their ability to generate high-valent manganese (IV)-oxo species. Generation of high-valent metal-oxo porphyrins was dependent on two methods: chemical and photo generation. Chemical methods rely on the use of a new, sacrificial oxidant iodobenzene diacetate PhI(OAc)2 to generate MnIV(Por)O intermediates from a MnIII(Por)Cl precursor. Photogeneration of high-valent manganese-oxo porphyrin intermediates from visible light irradiation relied on the use of silver salts to generate photo-labile precursors.