

New Catalytic Reactions of Iron(III) Porphyrins

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ABSTRACT

Metalloporphyrins have long been known to be effective catalysts for a variety of organic reactions. These include cyclopropanation, epoxidation, and aziridination of olefins. Iron porphyrins are also efficient catalysts for the olefination of aldehydes and ketones in the presence of triphenylphosphine. This suggested to us that iron porphyrins might have the potential to mediate a variety of other processes. The work described in this dissertation broadly extends the reactions catalyzed by iron(III) tetraphenylporphyrin chloride by focusing on the use of metalloporphyrins, mainly iron(III), Fe(TPP)Cl, as catalysts for N-H, C-H and O-H insertion reactions and cyclopropanation of arenes using various diazo reagents as sources of carbenes. A tandem N-H insertion/cyclization reaction using ethylenediamine and ethanolamine to give 2-piperazinone and 2-morpholinone respectively has also been investigated. Fe(TPP)Cl is one of the most efficient catalysts for insertion of the carbene derived from EDA into amine N-H bonds. This insertion reaction can be performed at room temperature and atmospheric conditions in relatively short reaction times. Fe(TPP)Cl is also an effective catalyst for O-H insertion reactions to alcohols when substituted methyl 2-phenyldiazoacetates are used as sources of carbene. Aromatic and normal aliphatic alcohols give O-H insertion as the only product.