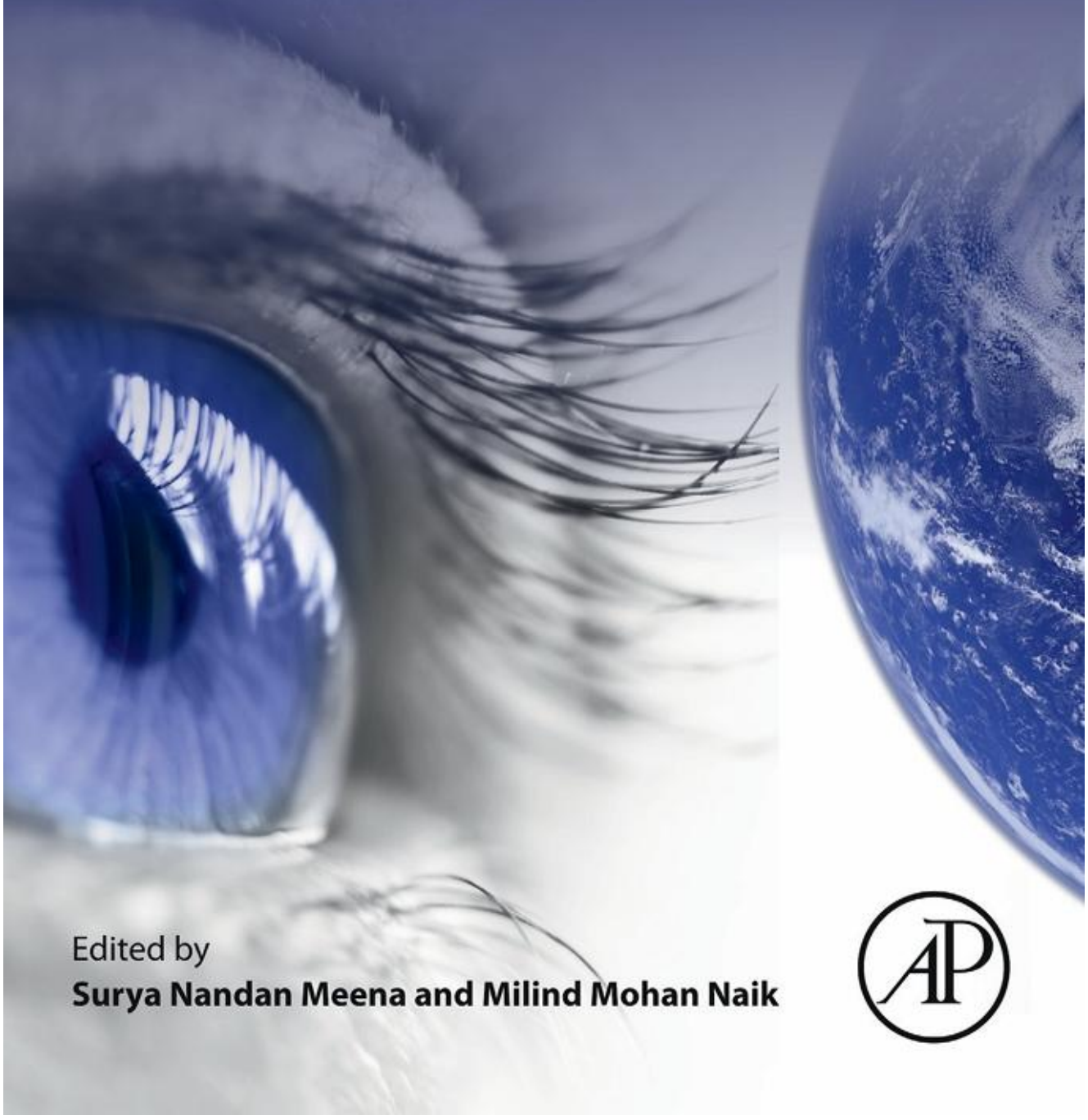
Advances in Biological Science Research

A Practical Approach



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Contents

Chapter 22

Iron-oxygen intermediates and their applications in biomimetic studies

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22.1 Introduction

The controlled oxidation of organic compounds by activating dioxygen carried out by metals is required for the key metabolic functions, such as the repair of RNA and DNA, in plants the desaturation of fatty acids, hydroxylation of methane in methanotrophs, biosynthesis of β-lactam antibiotics, and the formation of blood vessels for sensing of hypoxia [1−5]. Developing oxidation reactions that use renewable and environment friendly oxidants has become very important as oxidation reactions are critical for numerous chemical transformations [6,7]. A variety of biological reactions carried out by metalloenzymes utilize dioxygen (O_2) molecule. These enzymes perform oxidative reactions like epoxidation, halogenation, *cis*-dihydroxylation, and N-dealkylation by activating O_2 using a variety of active sites containing nonheme and heme copper, iron, and other metals [8].

A large number of enzymes employ iron centers to carry out metabolically vital oxidative transformations by activation of O_2 molecule [1,3]. Iron center coordinated to 2-His-1-carboxylate facial triad motifs [9−12] are utilized by most of these enzymes to catalyze substrate oxidations, including epoxidation, desaturation, *cis*-dihydroxylation, and halogenation. Commonly used reductants like NADH (nicotinamide adenine dinucleotide), tetrahydrobiopterin (THB) [13,14], α-ketoglutarate (α-KG) [3], and ascorbate [15,16] are used as electron donors for O_2 activation. For these enzymes, a $Fe^{IV}(O)$ species is postulated as an active oxidant; for Rieske dioxygenase, which catalyzes *cis*-dihydroxylation of arene, *cis*-HO-$Fe^{V}O$ is proposed as the oxidant [1,17,18].

The iron containing cytochromes P450 (CYP 450) of the heme-based monooxygenase are an important and versatile group with wide applications for human health and known to perform biosynthesis of hormones, the

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