

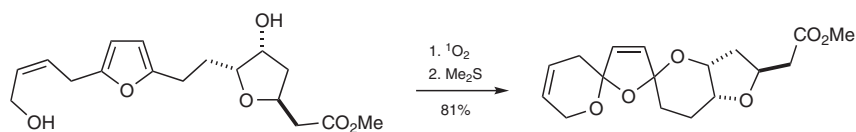
Abstracts

p 7

2.1 Photocatalytic Oxidation

A. G. Griesbeck, S. Sillner, and M. Kleczka

In this chapter, the transfer of molecular oxygen to organic substrates initiated by the action of an electronically excited catalyst with a substrate molecule or with triplet oxygen is described. Most of the primary products that derive from these reactions have an intact oxygen–oxygen bond (i.e., they are peroxides, hydroperoxides, or acyclic/cyclic dialkyl peroxides) or they are, in subsequent steps, converted into reduced products such as alcohols, ethers, or carbonyl compounds.



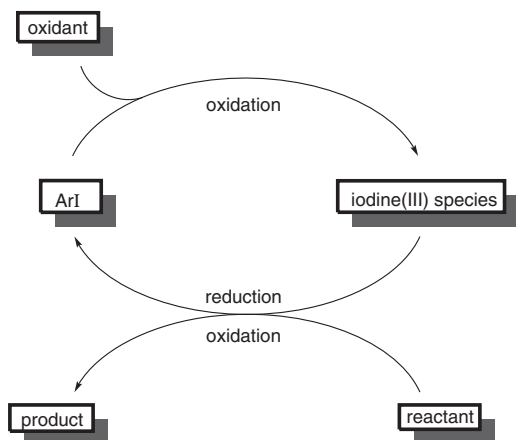
Keywords: alkenes · allylic alcohols · catalysts · hydroperoxides · oxygenation · peroxides · photochemistry · photooxidation · porphyrins

p 29

2.2 Catalytic Oxidations with Hypervalent Iodine

F. V. Singh and T. Wirth

Hypervalent iodine chemistry is a very active research area in both organic synthesis and natural product chemistry. Hypervalent iodine reagents have been used to perform various oxidative transformations under mild reaction conditions. These reagents have received particular attention since the first reports, in 2005, that they can act as catalysts. Since then, various hypervalent iodine catalyzed oxidative functionalizations, such as oxidations of alcohols and phenols, α -functionalizations of carbonyl compounds, cyclizations, and rearrangements have been successfully achieved. Several catalytic reactions have been developed using hypervalent iodine reagents as catalysts, while in other reactions iodoarenes have been used as precatalyst to generate active iodine(III) or iodine(V) species in situ. This chapter highlights various aspects of hypervalent iodine-catalyzed oxidation reactions, including asymmetric variants.



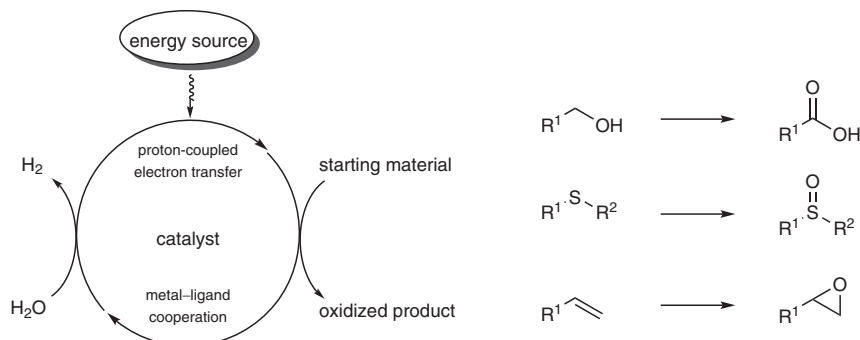
Keywords: catalytic oxidations · hypervalent iodine reagents · oxidants · stereoselective reactions

p 63

2.3 Water as an Oxygen Source for Oxidation Reactions

P. Garrido-Barros, I. Funes-Ardoiz, P. Farràs, C. Gimbert-Suriñach, F. Maseras, and A. Llobet

The use of water as oxygen source for the catalytic oxidation of organic substrates is a clean alternative to the commonly used methods that utilize oxidizing agents based on contaminant metals such as chromium or manganese. In this chapter, a detailed description of the thermodynamic requirements of this type of reaction is given, with particular emphasis on the so-called organic-substrate-assisted water splitting (OSA-WS) reaction that generates hydrogen gas as the only byproduct of the reaction. Important considerations regarding the metal catalyst needed to perform these reactions are discussed, followed by specific examples described in the literature. Among them, are examples of epoxidation of alkenes, oxidation of sulfides to sulfoxides, and oxidation of alcohols to the corresponding carboxylic acids. In some cases, the energy input to perform the reaction comes from visible light by using photosensitizers or semiconductors as light-harvesting agents. Finally, two examples of photoelectrochemical cells (PECs) are described, where light-induced oxidation and reduction half reactions take place in separate compartments. This design provides an easy-to-process reaction where the oxidized organic compound and hydrogen gas byproduct are generated in independent compartments, and at the same time avoids undesired side reactions that may occur as a result of the mixture.



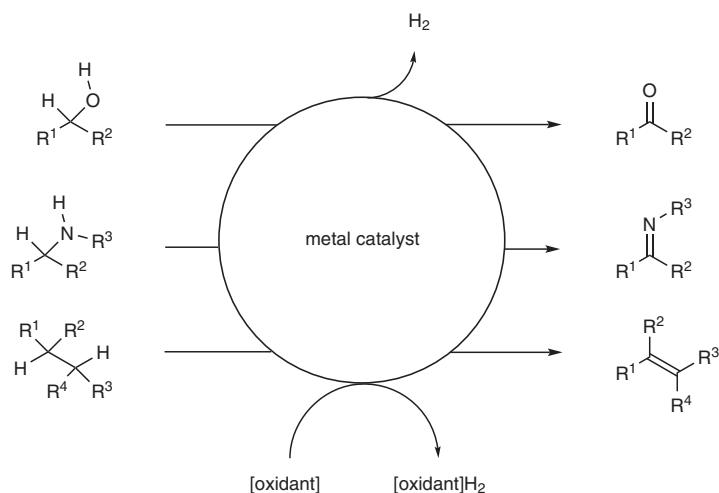
Keywords: water · oxidation · catalysts · sulfides · sulfoxides · alcohols · alkenes · epoxidation · styrene · light as energy source · photosensitizers · semiconductors · green chemistry · atom economy · proton-coupled electron transfer (PCET) · ruthenium–aqua complexes · pincer ligands · metal–ligand cooperation

p 81

2.4 Dehydrogenation

Y. Kayaki and T. Ikariya

This chapter highlights effective dehydrogenation from saturated polar and non-polar molecules, including alcohols, amines, and (functionalized) alkanes, using homogeneous transition-metal complexes as catalysts. In the context of significant advances in molecular catalysts with metal–ligand cooperation as the key dehydrogenation strategy for the promotion of H^+ and H^- transfer, selected examples of dehydrogenative oxidation in the presence or absence of sacrificial oxidants are reviewed. As synthetic applications of catalytic dehydrogenation, oxidative coupling reactions with alcohols and/or amines are also presented.



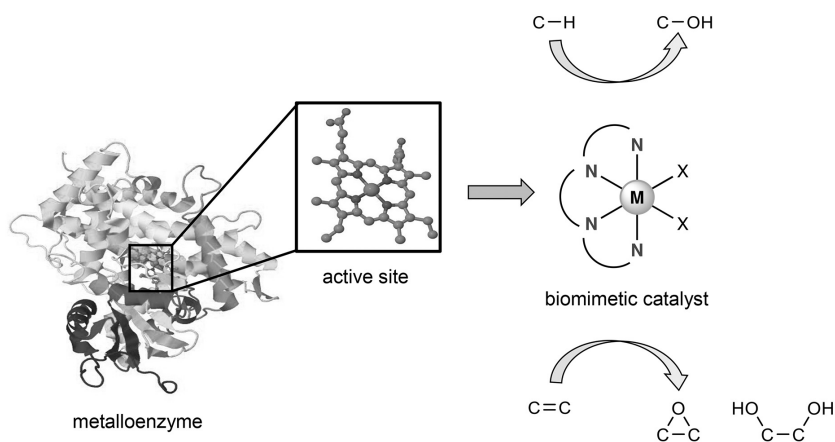
Keywords: alcohols · alkanes · amines · carbonyl compounds · dehydration · dehydrogenation · heterocycles · homogeneous catalysis · hydride abstraction · hydrogen transfer · oxidative coupling · transition metals

p 113

2.5 Biomimetic Oxidation in Organic Synthesis

L. Vicens, M. Borrell, and M. Costas

Oxidation reactions performed by metalloenzymes are regarded as a model for the development of novel methods that could represent a more sustainable alternative to traditional oxidants, or that could also introduce novel selectivity. Herein, are collected oxidation methodologies that reproduce reactivity aspects of enzymatic systems and that find use for synthetic purposes. This includes catalytic systems based on iron, manganese, and copper that allow for the functionalization of aliphatic C–H bonds leading to halide and pseudohalide insertion, the epoxidation and *cis*-dihydroxylation of alkenes, the oxidation of alkanes, the oxidation of alcohols, and the hydroxylation of phenols.

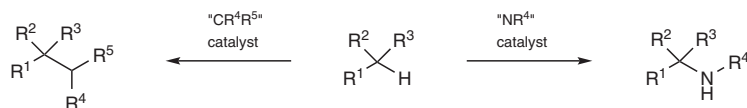


Keywords: alkane oxidation · alkane halogenation · alkane fluorination · epoxidation · *cis*-dihydroxylation · hydrogen peroxide · phenol oxidation · alcohol oxidation · copper catalysts · iron catalysts · manganese catalysts

3 Metal-Catalyzed Oxidation of Alkanes To Give Esters or Amines

A. Caballero, M. M. Díaz-Requejo, and P. J. Pérez

The modification of relatively unreactive alkanes of general formula C_nH_{2n+2} , as well as of cycloalkanes C_nH_{2n} , by oxidation of C–H bonds in a catalytic manner is reviewed, focusing on their direct conversions into esters or amines upon incorporation of carbene or nitrene fragments, respectively.

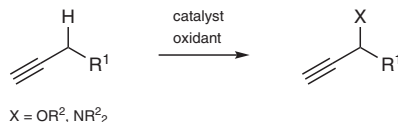
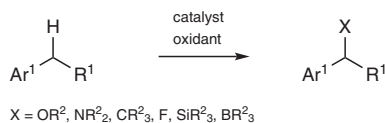
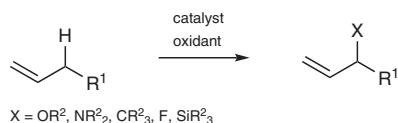


Keywords: alkanes • carbene insertions • nitrene insertions • homogeneous catalysts • esters • amines • organometallic complexes

4 Allylic, Benzylic, and Propargylic Oxidation

P. Chen and G. Liu

Oxidation reactions of C–H bonds are fundamental in modern organic synthesis and always attract much attention. Over the last three decades, remarkable progress in the oxidation of allylic and benzylic C–H bonds has been made, whereas only a few examples of the oxidation of propargylic C–H bonds have been reported. In this review, the catalytic oxidation of allylic, benzylic, and propargylic C–H bonds is summarized. It covers the construction of C–O, C–N, C–C, and C–F bonds. Some rare examples of C–B and C–Si bond formation in benzylic oxidations are also included.



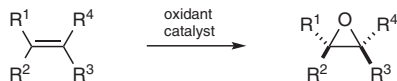
Keywords: catalysts • allylic oxidation • benzylic oxidation • propargylic oxidation • amination • alkylation • arylation • fluorination • silylation • borylation

5.1 Epoxidation of Alkenes

A. Berkessel, H. Engler, and T. M. Leuther

The Sharpless, Jacobsen/Katsuki, and Shi epoxidations are frequently applied in the asymmetric epoxidation of relatively electron-rich alkenes. The development and application of these “classics” has been reviewed numerous times. This chapter covers recent advances

ces in the field, e.g. with regard to the extension of asymmetric epoxidation catalysis to hitherto problematic substrate classes, such as non-conjugated terminal alkenes, or homo- and bis-homoallylic alcohols. At the same time, hydrogen peroxide continues to receive increasing attention as an environmentally friendly and economically attractive terminal oxidant. Examples of efficient organocatalytic epoxidation processes are summarized as well. For electron-poor alkenes, e.g. those carrying carbonyl, nitrile, or sulfone acceptor groups, quite remarkable progress has recently been made both in metal and organocatalysis, and the chapter also includes details of methods and protocols in this area.



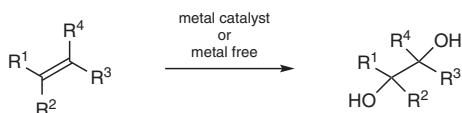
Keywords: alkenes · oxidation · oxiranes · epoxidation · catalysts · enantioselectivity · iron catalysis · manganese catalysis · ruthenium catalysis · titanium catalysis · tungsten catalysis · vanadium catalysis · zirconium catalysis · organocatalysis · enzyme catalysis

p 309

5.2 Dioxygenation of Alkenes

C. Martínez and K. Muñiz

A plethora of natural products exist that contain characteristic vicinal 1,2-diols in their scaffolds. The alkene dihydroxylation methodology developed by Sharpless continues to be the most robust and general method to obtain this important motif. However, the main problem with this transformation is the use of osmium as the catalyst and, since the 1990s, various methods have been developed that employ alternative transition metals. In this chapter, the most important protocols for the racemic and enantioselective dioxygenation of alkenes mediated by metals are summarized, together with recently developed methods that employ chiral nonracemic hypervalent iodine(III) reagents.



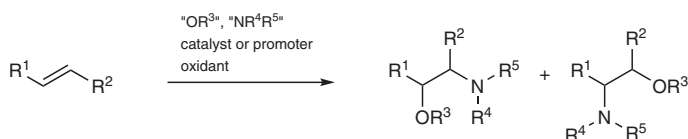
Keywords: oxidation · dihydroxylation · alkenes · enantioselectivity · catalysis · osmium tetroxide · osmium(VIII) oxide · diols · hypervalent iodine(III)

p 343

5.3 Aminohydroxylation and Aminoxygenation of Alkenes

S. R. Chemler and T. Wdowik

The aminohydroxylation of alkenes provides β -amino alcohols (vicinal amino alcohols). A number of alkene aminohydroxylation protocols (and those of related reactions termed oxyamination and aminoxygenation), predominantly enabled by transition-metal catalysis, are described in this chapter, which focuses on literature published in the period 1996–2015. Cyclic and acyclic compounds containing vicinal amino alcohols and derivatives thereof can be prepared from alkenes with good regio-, diastereo-, and enantioselectivity.



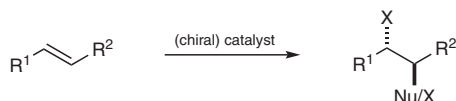
Keywords: alkenes · aminooxygenation · aminohydroxylation · oxyamination · β -amino alcohols · catalysis · osmium catalysts · iron catalysts · rhodium catalysts · copper catalysts · palladium catalysts · manganese catalysts

p 389

5.4 Halogenation and Halocyclization of Alkenes

A. Andries-Ulmer and T. Gulder

Halogenated compounds are of high importance in many disciplines, even beyond chemistry. The unique properties that can be traced back to the halogen atom make the development of methods for selectively installing carbon–halogen bonds a rewarding goal. This chapter provides an overview of effective methods for the chemo-, regio-, and, in particular, stereoselective formation of C–X bonds using different oxidative approaches.



X = Cl, Br, I

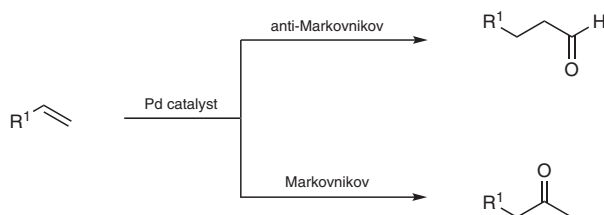
Keywords: halogenation · halocyclization · dihalogenation · organocatalysis · hypervalent iodine · ion pairing · phosphoric acids · C_3 -symmetric trisimidazolines · amino ureas · Lewis base catalysis · hydrogen bonding · carbamates · thiocarbamates · dimeric cinchona alkaloids · Lewis acid catalysis · titanium · scandium

p 429

5.5 The Wacker Process

N. J. Race, H. H. Patel, and M. S. Sigman

The palladium-catalyzed Wacker process has been extended toward the oxidation of substituted α -alkenes and internal alkenes. Methods providing access to Markovnikov and anti-Markovnikov products in high selectivity are discussed.



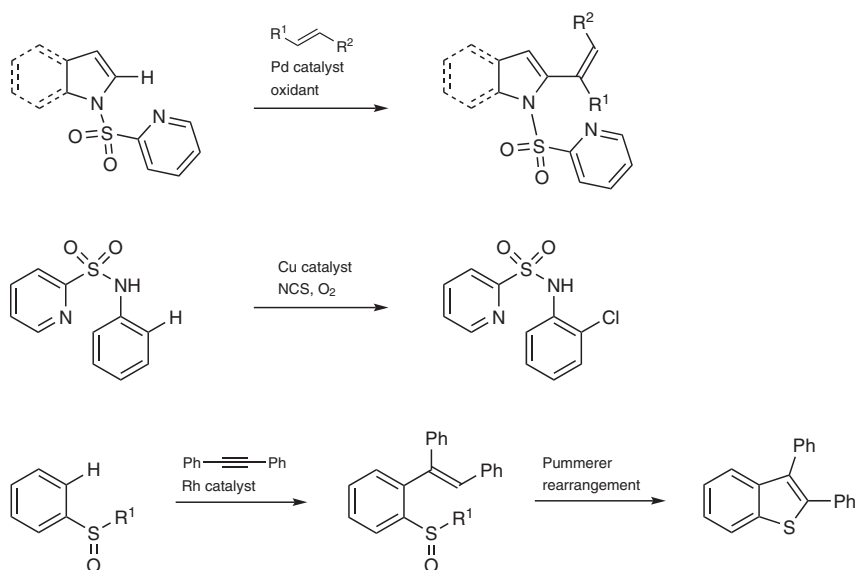
Keywords: Wacker oxidation · palladium catalysis · aldehyde-selective · ketone-selective · Markovnikov · anti-Markovnikov · oxidation · alkenes

p 449

6 Sulfinyl- and Sulfonyl-Containing Directing Groups in C–H Oxidation of Arenes

R. Gómez-Arrayas and N. Rodríguez

Although sulfur-containing directing groups, such as sulfoxides or sulfones, have only recently been employed as directing groups in C–H functionalization reactions, they have proved to be powerful tools for assisting metallacycle formation to ensure regiocontrol in a wide variety of transformations. Furthermore, the chemical versatility associated with these groups not only allows for their facile and high-yielding removal, but also provides an additional handle for the diversification of the resulting products.



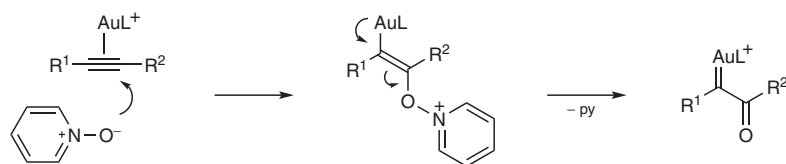
Keywords: C–H functionalization • directing groups • sulfoxides • sulfones • sulfonamides • arenes • heteroarenes • transition-metal catalysis • arylation • alkenylation • cyclization

p 479

7 Gold-Catalyzed Oxidation of Alkynes

P. Calleja, R. Dorel, and A. M. Echavarren

This chapter reviews gold-catalyzed inter- and intramolecular oxidative reactions of alkynes proceeding through α -oxo gold(I) carbenes or related intermediates. Oxidative reactions of enynes and applications of gold-catalyzed oxidative reactions in total synthesis are also covered.



Keywords: gold • alkynes • enynes • cyclizations • carbenes • *N*-oxides • sulfoxides • nitrones

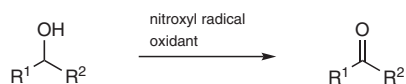
p 529

8.1 Recent Developments in Catalytic Alcohol Oxidation Using Nitroxyl Radicals

L. M. Dorman, N. L. Hughes, and M. J. Muldoon

This chapter describes the use of nitroxyl radicals as catalysts for the oxidation of alcohols, with a focus on recent developments in this area. Stable nitroxyl radicals can be used with a variety of different terminal oxidants and the methods discussed have a much greater substrate scope compared to precious-metal catalysts. The methods are readily accessible for small-scale applications as they use commercially available reagents and do not require high pressures or temperatures. This review not only describes the selective oxidation of alcohols to aldehydes, ketones, and carboxylic acids, but also reac-

tions where alcohol oxidation is a key step, such as the oxidative synthesis of nitriles, imines, and amides.



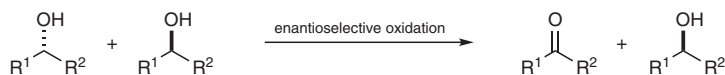
Keywords: alcohols · aldehydes · amides · amino alcohols · carboxylic acids · hydroxy acids · imines · ketones · keto acids · lactones · nitriles

— p 569 —

8.2 Enantioselective Oxidation of Alcohols

B. M. Stoltz, A. C. Wright, D. C. Ebner, and N. Park

Described herein is a review of methods for the enantioselective oxidation of alcohol derivatives to afford enantioenriched alcohols from the corresponding racemates. This review emphasizes recent discoveries in the field, i.e. those that have been reported since 2011. Topics covered include transfer hydrogenation, aerobic metal catalysis, nitroxyl-based radical catalysis, manganese catalysis, and biocatalysis.



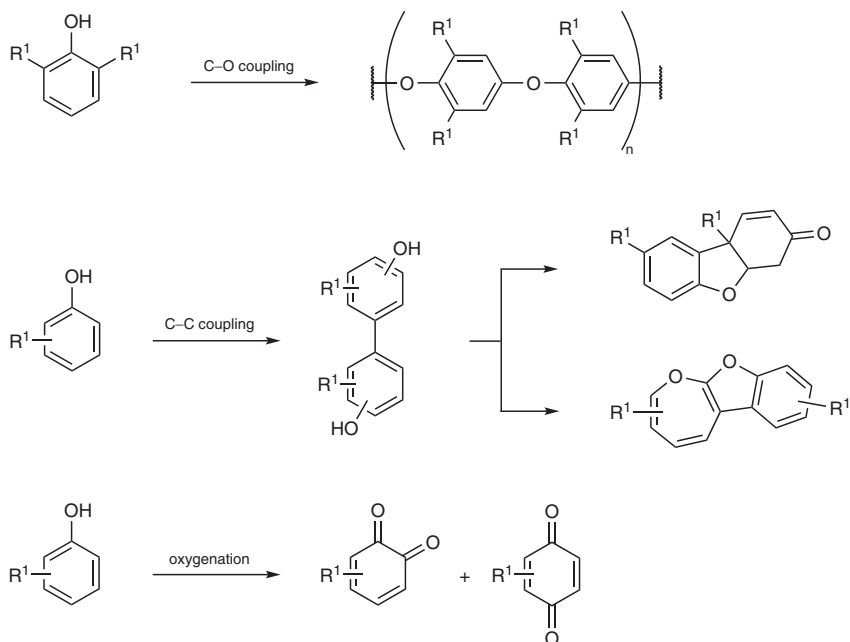
Keywords: alcohols · carbonyl compounds · oxidation · enantioselectivity · stereoselectivity · kinetic resolution · desymmetrization · transfer hydrogenation · aerobic metal catalysis · nitroxyl-based radical catalysis · manganese catalysis · iridium catalysis · palladium catalysis · ruthenium catalysis · iron catalysis · vanadium catalysis · biocatalysis

— p 587 —

9 Catalytic Aerobic Oxidation of Phenols

J.-P. Lumb and K. V. N. Esguerra

Phenols are ubiquitous motifs in nature and their aerobic oxidation is implicated in the biosynthesis of a wide variety of biologically relevant compounds and polymeric materials. This chapter outlines notable catalytic aerobic oxidations of phenols, and includes recent advances in oxidative dimerizations, polymerizations and oxygenation reactions as well as key advances in copper-mediated phenol functionalization. Specifically, this chapter focuses on the synthesis of poly(1,4-phenylene oxides), biphenols, quinones, Pummerer's ketones, and oxepinobenzofurans.



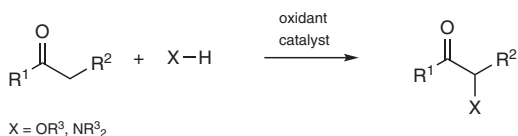
Keywords: phenols · tyrosinase · benzofurans · poly(1,4-phenylene oxides) · biphenols · *ortho*-quinones · *para*-quinones · Pummerer's ketone · oxepinobenzofurans · *ortho*-amino-phenols · copper · aerobic

p 635

10 α -Oxidation of Carbonyl Compounds

M. Uyanik and K. Ishihara

The α -heterofunctionalization of carbonyl compounds enables access to a large number of synthetic building blocks and high-value molecules. This chapter describes the direct catalytic α -oxidative coupling of carbonyl compounds with oxygen- and nitrogen-based reagents.



Keywords: α -oxidation · transition-metal catalysis · organocatalysis · hypervalent iodine · hypoiodite · carbonyl compounds · α -oxygenation · α -amination · enantioselective

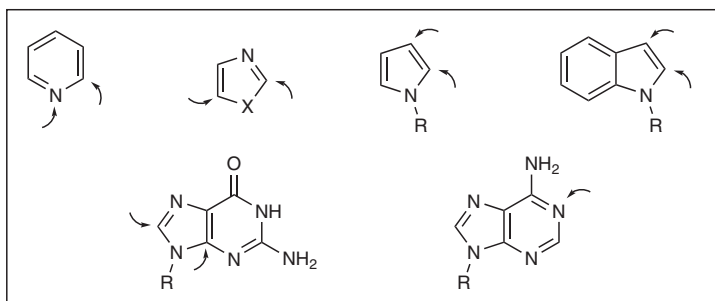
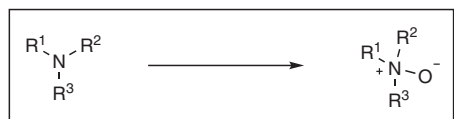
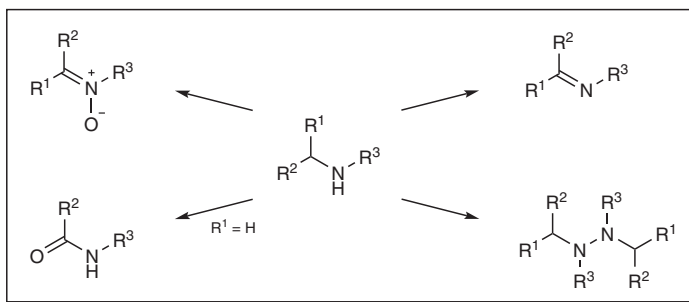
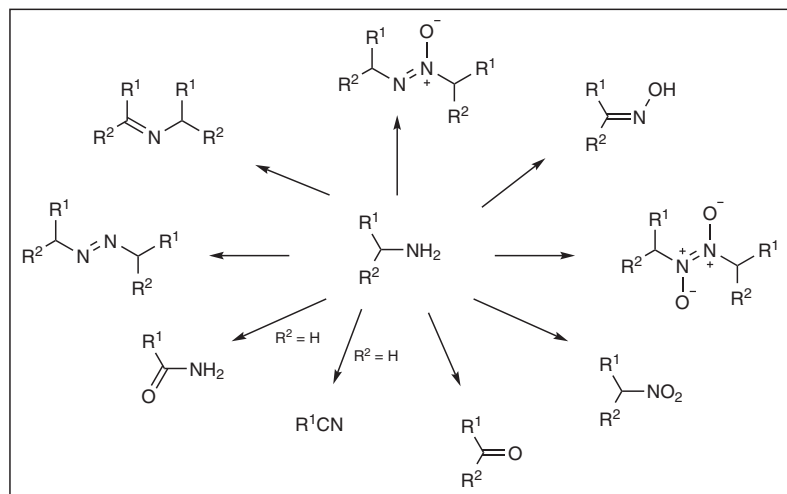
p 671

11 Oxidation of Amines and N-Hetarenes

N. Jiao and Z. Li

The oxidation of amines and hetarenes are significant transformations that have been widely applied in synthetic organic chemistry. In this chapter, the oxidation of primary, secondary, and tertiary amines, affording imines, nitriles, amides, carbonyls, oximes, nitro compounds, diazenes and their oxides, nitrones, hydrazines, and *N*-oxides, as well as the oxidation of hetarenes including pyridines, azoles, pyrroles, indoles, guanines, and adenines, are comprehensively discussed. In addition to traditional organometallic catal-

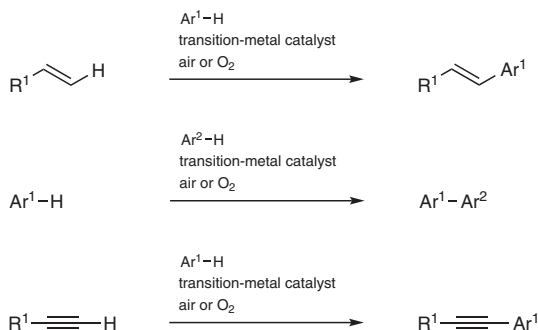
ysis to fulfill these oxidation reactions, some advanced approaches such as photocatalysis, biochemical catalysis, and biomimetic catalysis are also described.



Keywords: oxidation of amines · oxidation of hetarenes · organometallic catalysis · photocatalysis · biomimetic catalysis

12 Aerobic Oxidative Intermolecular Cross-Coupling and Heck Reactions*F. Bellina and L. A. Perego*

Transition-metal-catalyzed aerobic oxidative C–C bond forming couplings allow the synthesis of alkenyl-, (het)aryl-, and alkynyl-substituted (het)arenes by activation of C–H bonds on both of the reaction partners.



Keywords: C–H activation · C–C bond formation · aerobic oxidation · oxidative coupling · Fujiwara–Moritani reaction · oxidative Heck reaction · dehydrogenative coupling · palladium · copper · green chemistry · regioselectivity · arenes · hetarenes · alkenes