

PREFACE TO VOLUME 74

Although not by design, Volume 74 comprises three chapters that represent two of the most fundamental processes in organic chemistry, namely, oxidation and reduction. In fact, 31 of the 241 chapters published in *Organic Reactions* are dedicated to the oxidation or reduction of organic compounds in some form. Thus, our three newest chapter family members are in good company.

The first chapter by Hans-Ulrich Blaser and Felix Spindler covers the catalytic, enantioselective hydrogenation of the azomethine function including imines, activated imines, oximes, hydrazones, and azacycles to form enantiomerically enriched amines. Organic compounds containing nitrogen atoms on one or more stereogenic centers are ubiquitous in nature and are of unparalleled importance in pharmaceutical substances. From amino acids and amino sugars to alkaloids and penicillins, chiral nitrogen-containing compounds are of significant synthetic and biological interest. Because chiral amines were traditionally available from classical resolution, the development of general methods for the enantioselective construction of stereogenic carbons bearing nitrogen substituents lagged behind that for the synthesis of chiral alcohols. Whereas catalytic, asymmetric hydrogenation of alkenes and carbonyl compounds is now a well-established process, the development of catalysts for production of enantiomerically enriched amines by hydrogenation of azomethines has only recently reached a level of practicality and selectivity that rivals those for carbonyl compounds. Blaser and Spindler clearly outline the unique challenges associated with the formation and reduction of imines and the currently available solutions. As is often the case, the selection of the appropriate transition metal, ligand and reaction conditions is crucial for success and these authors provide expert guidance from their extensive practical knowledge.

The second chapter by James M. Bobbitt, Christian Brückner, and Nabyl Merbouh covers the use of oxoammonium salts and nitroxides as catalysts for the oxidation of alcohols. The discovery of stable nitroxide-based free radicals opened many opportunities for their use as ESR spin labels in medicine. However, their impact in synthetic organic chemistry has been primarily as mild and selective catalysts for the oxidation of alcohols in the presence of a stoichiometric amount of a secondary oxidant. Bobbitt, Brückner, and Merbouh have critically distilled the vast literature on the most important practical aspects of these oxidations such as the choice of nitroxide (often the familiar TEMPO), the choice of stoichiometric oxidant such as hypochlorite, chlorite, peroxides, iodine(III) agents, and oxygen (in the presence of metal co-catalysts), and the importance of the medium (acidic or basic). The use of metal-free oxidations (particularly on large scale) benefits from a more selective oxidation process and a less toxic waste stream. Of special note is the ability of this method to prepare enantiomerically enriched aldehydes bearing configurationally labile stereogenic centers without racemization. The authors thoroughly cover the practical advances available for

this method including the use of polymer-supported reagents, reactions in ionic liquids, and applications to sensitive carbohydrates and nucleosides.

The third chapter by Michael J. Porter and John Skidmore covers the asymmetric epoxidation of alkenes bearing electron-withdrawing groups. The synthetic utility of epoxides cannot be overstated and indeed, no fewer than five *Organic Reactions* chapters are concerned with the synthesis or transformations of oxiranes. However, the special challenges associated with oxidizing electron-deficient alkenes requires alternative solutions compared to normal, electron-rich alkenes. Whereas the asymmetric epoxidations of allylic alcohols and isolated alkenes have general solutions, the currently available methods for, inter alia, unsaturated ketones, aldehydes, esters, nitriles, and sulfones are much more varied. Accordingly, the thorough and focused presentation provided by Porter and Skidmore represents a welcome addition to this rapidly expanding field. The authors present a scholarly overview of the wide range of methods available and the various mechanistic and stereochemical attributes of each (ranging from the use of polypeptides, to transition metal catalysts to phase transfer catalysts to dioxiranes). The authors then describe the enantioselective oxidations of all the classes of substrates organized by functional group. This presentation will be of tremendous utility to the experimentalist hoping to apply this method to a given target. In view of the diversity of reagents used for these oxidations, the experimental conditions and representative procedures are particularly valuable. Together with the chapter on the Katsuki-Sharpless oxidation by Tsutomu Katsuki and Victor S. Martin (Volume 48) and the chapter on dioxirane epoxidations by Waldemar Adam, Chantu R. Saha-Möller, and Gong-Gui Zhao (Volume 61), this chapter provides coverage of all three major classes of alkenes that can be converted to enantiomerically enriched epoxides.

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