

## PREFACE TO VOLUME 80

The Preface to Volume 76 highlighted the enormous impact of transition-metal catalysis in synthetic organic chemistry. Three of the last ten Nobel Prizes in Chemistry have been awarded for the discovery and development of transition-metal-catalyzed reactions that fundamentally changed the practice of organic synthesis (2001: reduction/oxidation (Knowles, Noyori, and Sharpless); 2005: olefin metathesis (Chauvin, Grubbs, Schrock); 2010: cross coupling (Heck, Negishi, Suzuki)). The three reviews in that volume raised the number of chapters in *Organic Reactions* dedicated to transition metal catalysis to 17 since Volume 50. This volume adds two more chapters to that number both of which feature catalysis with rhodium. Rhodium has played a pivotal role in the history of (asymmetric) catalysis thanks to the pioneering contributions of William S. Knowles, who developed the use of chiral rhodium hydrogenation catalysts for the industrial synthesis of L-DOPA which earned him a Nobel Prize in 2001. To celebrate Knowles' contributions (who sadly passed away in June 2012) we dedicate this volume to his memory.

The first chapter by Michael P. Doyle, Yu Liu, and Maxim Ratnikov describes use of chiral rhodium complexes to effect catalytic, asymmetric carbon–hydrogen insertion reactions intramolecularly. The advent of C–H functionalization reactions as useful and predictable transformations is one of the major areas of current research in synthetic organic and organometallic chemistry. Professor Doyle and his research group have pioneered the development of specialized catalysts for effecting reactions of diazo compounds as precursors for the carbenoid intermediates responsible for the functionalization of double bonds (by cyclopropanation) and carbon–hydrogen bonds (by insertion). This excellent chapter details the structural scenarios in which diazocarbonyl compounds can be generated and activated to form, *inter alia*, lactones, lactams, and cyclic ketones. In many cases, the site selectivity of insertion to specific C–H bonds is extremely high as is the selectivity for insertion to enantiotopically related hydrogens. The usefulness of this process has been demonstrated by its application as a strategy level transform in total synthesis endeavors. This chapter constitutes the perfect complement to the chapter on carbon–carbon bond formation by catalytic, asymmetric, *intermolecular* C–H insertions by Davies and Pelphrey that appeared in Volume 75.

The second chapter by David M. Hodgson, Agn s H. Labande, and Sengodagounder Muthusamy also describes the use of (chiral) rhodium complexes in combination with diazocarbonyl compounds, but in this case to effect a remarkable transformation that dramatically increases the molecular complexity of the substrates. The rhodium carbenoids generated in this reaction are intercepted by carbonyl groups within the molecule (ketones, esters, amides) to form carbonyl ylides, a relatively rare class of 1,3-dipoles. These ylides are extremely reactive and combine rapidly with dipolarophiles to form oxapolycyclic products.

Owing to the high reactivity of carbonyl ylides, many types of dipolarophiles can be engaged, including alkenes, alkynes, imines, and carbonyl compounds. In the intermolecular mode, the [3+2] cycloadditions take place with high regio- and diastereoselectivity; however, in the intramolecular mode the complexity-generating power of this transformation is truly staggering. Linear molecules containing both the carbonyl ylide precursor and the dipolarophile transform themselves into oxatricyclic compounds with astonishing facility and stereoselectivity. The diversity of ring sizes and substitution patterns that can be generated naturally leads to many creative applications in the synthesis of polycyclic natural products. Moreover, the use of chirally modified rhodium catalysts allows the enantioselective construction of these complex architectures with high levels of stereocontrol. The Hodgson laboratories have been at the forefront of many developments in the tandem cycloaddition chemistry of carbonyl ylides, and we are extremely fortunate that such world-class experts have contributed a comprehensive and scholarly treatment of the field.

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