

PREFACE TO VOLUME 82

The two chapters in Volume 82 describe reactions that involve one of the most common transformations in organic chemistry, namely, the pairwise combination of double-bonded functional groups. The importance of this enormous family of reactions is a reflection of the spectacular diversity of precursors and products that can arise from appropriate modulation of reactivity of the partners and especially selection of reagents that dictate the outcome.

The first chapter authored by Takeshi Takeda and Akira Tsubouchi describes the combination of carbonyl compounds in the presence of highly reactive, low-valent titanium reagents in the classic McMurry reaction. This remarkable process generates alkenes from two oxygenated functional groups, generally aldehydes and ketones (and their equivalents), but also more recently, esters, amides, and carboxylic acids. Although this transformation seems to decrease the chemical potential of the reactants, it has been extensively employed in the synthesis of hindered and strained alkenes and in particular for molecules with higher dimensionality (cyclophanes, helicenes, and highly conjugated compounds) by virtue of the highly exothermicity of the process. Applications in the total synthesis of natural products are also well represented. Recent advances include strategies for the olefination of different partners in both inter- and intramolecular reactions. Perhaps the most important insights that Takeda and Tsubouchi provide our readers is a discussion of the myriad combinations of titanium halides with reducing agents and additives as well as a thorough coverage of low-valent metals other than titanium for this process. These concoctions generally afford heterogeneous mixtures of the active agent that inevitably lead to irreproducibility. However, the detail provided for generating these reactive metals are sure to allow much more reliable reduction to practice. Reading this chapter gives one an appreciation of the striking diversity of complex molecular architectures whose synthesis has been enabled by this highly versatile name reaction.

The second chapter concerns the chemistry of highly reactive, double-bonded functional groups, namely ketenes. The electronic structure of these cumulenes enables facile combination with other double-bonded functional groups in [2+2] and [4+2] cycloadditions. Indeed, Chapter 2 in Volume 45 contained a comprehensive review of ketene cycloadditions authored by John A. Hyatt and Peter W. Reynolds. Now, nearly 20 years later, the field has advanced considerably to the point where ketenes undergo highly enantioselective [2+2] and [4+2] cycloadditions with carbonyl azomethine partners. Critical to the success of the asymmetric catalysis has been the development of chiral Lewis acids and Lewis bases that can activate the various reaction components in such a way as to produce highly enantiomerically enriched β -lactones and β -lactams. We are fortunate that one of the pioneers in the development of these asymmetric processes, Prof. Scott G. Nelson, together with coauthors Robert D. Dura and Timothy J. Peelen, have

composed a thorough disquisition on the state of art of these remarkable transformations. The wide range of catalysts available for this process can present challenges for the practitioner to select the optimal agent and conditions for a given pair of reactants. Thus, the comprehensive coverage of many pairwise combinations and the guidelines for selection of the best starting point provided by these authors are of particular merit. The significant synthetic potential of the products and the high levels of stereocontrol available for their construction assure that this chapter will find widespread use in academic and industrial laboratories alike.

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