

PREFACE TO VOLUME 79

One of the hallmarks of the *Organic Reactions* series is the critical and comprehensive coverage that each chapter provides to the practitioner of organic synthesis. However, in a larger sense, the series endeavors to comprehensively encompass the various incarnations of useful transformations. The two chapters in this volume satisfy that objective by expanding our franchise in two important processes, namely palladium-catalyzed cross-coupling and the chemistry of enolates.

The first chapter by Gary A. Molander and Ludivine Jean-Gérard describes the use of organotrifluoroborate salts in a modification of the Nobel Prize winning Suzuki-Miyaura cross-coupling reaction. The impact of this palladium-catalyzed transformation in academic and especially industrial organic synthesis cannot be overestimated. Boronic acid cross-coupling has evolved as the primary strategic disconnection for making carbon-carbon bonds. The major developments in this field over the past 15 years have been (1) the introduction of new families of ligands that have allowed for significantly milder reaction conditions with the attendant increase in functional compatibility, (2) the expanded scope of the coupling partners to include saturated carbon moieties, and (3) the introduction of boronic acid surrogates as robust cross-coupling partners. Organotrifluoroborates represent one of the most successful of the surrogates and have been employed in myriad applications thanks in large measure to their stability, ease of synthesis, and commercial availability. Professor Molander and his research team have been at the forefront of these efforts, and we are fortunate that he has provided an outstanding account of the special attributes of these reagents, in particular those derived from heteroatom-substituted carbons. As is true for all members of this family of transformations, the selection of reaction conditions is highly substrate dependent, and the guidelines provided here for catalyst, ligand, solvent, and additive are critical starting points for any new application. This excellent chapter on boron-based cross-coupling reactions joins two previous chapters on tin-based (Stille-Kosugi-Migita) and silicon-based (Hiyama-Denmark) cross-couplings contained in Volumes 50 and 75, respectively, to form a trilogy of the most commonly employed examples of this transformation.

The second chapter by Nigel S. Simpkins and Michael D. Weller describes the successful marriage of classic lithium enolate chemistry with the modern concepts and methods of asymmetric synthesis. The formation of lithium enolates by stoichiometric deprotonation with lithium amide bases revolutionized the chemistry of carbonyl compounds by allowing the controlled formation of highly reactive enolates in a site and geometrically defined manner. The subsequent transformations with electrophiles soon evolved into one of the most powerful workhorse reactions in organic synthesis. Beginning in the 1980's, pioneering studies from the laboratories of Whitesell and Koga introduced the use of chiral lithium amide bases to effect enantioselective deprotonations of achiral and

meso epoxides and carbonyl compounds. Extensive developments in the Simpkins laboratories led to highly selective and in some cases catalytic, asymmetric deprotonations and subsequent transformations. This excellent chapter represents the state of the art in effecting asymmetric deprotonations of a variety of compounds through enantiotopic (internal) and enantiomorphic (external) selection processes. Recent advances include the selective deprotonation of non-carbonyl containing substrates such as benzylic deprotonation of (η^6 -arene)chromium complexes, phosphine oxides, and benzamides. Applications in asymmetric total synthesis have also been described.

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