

PREFACE TO VOLUME 93

Boron has all the best tunes

A. J. Downs in

“Chemistry of Aluminum, Gallium, Indium and Thallium”

It is ironic that a book dedicated to the chemistry of the heavier elements in Group 13 would bemoan the dominance of the lightest, boron. The reality is, however, that for applications in synthetic chemistry, boron is unparalleled in its versatility to facilitate the formation of new carbon-carbon and carbon-heteroatom bonds in myriad structural settings with extraordinary generality and selectivity.

Undoubtedly, the ease with which boron engages in so many diverse chemical transformations can be ascribed to its unique ability to exist in both tricoordinate and tetracoordinate constitutions and to interconvert between them with relative ease. As a consequence, boron can function as a Lewis acidic species (6 electron, neutral) and a Lewis basic species (8 electron, anionic), which enables both electrophilic and nucleophilic character to be expressed. No other element has such chemical virtuosity and the manifestations of its unique behavior continue to be developed. As a testimony to the remarkable and enduring impact of organoboron chemistry, it is worth noting that the 1979 Nobel Prize in Chemistry was shared by Herbert C. Brown and Georg Wittig “*for their development of the use of boron- and phosphorus-containing compounds, respectively, into important reagents in organic synthesis.*” Thirty-eight years later, there has been no surcease in advances.

One of the most frequently employed classes of organoboron compounds are boronic acids and their esters. In the past 30 years, boronic acids have emerged as one of the most capable placeholders for entry into dozens of catalytic cycles involving transition-metal catalysts. In this capacity, boron easily exchanges with various transition metals to deliver all manner of organic building blocks into constructive, bond forming cycles. Perhaps the most famous is the transmetalation to palladium in the Suzuki-Miyaura cross-coupling reaction (also recognized with a shared Nobel Prize in 2010).

In a landmark report in 1997, Tamio Hayashi and coworkers described another facile transmetalation of boronic acids to rhodium complexes to enable the conjugate addition of organic moieties to α,β -unsaturated carbonyl compounds. For decades, this powerful transformation, namely, 1,4-addition had been the purview of organocopper chemistry, but the difficulty in developing enantioselective variants hindered widespread application. With the discovery that readily available and shelf-stable boronic acids could serve as precursors, the development of enantioselective additions using chirally modified rhodium catalysts was very soon introduced.

Twenty years later, this reaction has achieved strategy level status, thanks to the efforts of many laboratories world-wide.

One of those laboratories is directed by Professor Hon Wai Lam (Nottingham, UK) who together with coworkers and coauthors Alan R. Burns and Iain D. Roy have taken on the enormous task of compiling the first, comprehensive disquisition on the entire scope and application of this tremendously powerful reaction. Professor Lam and his coauthors have constructed an outstanding chapter that encompasses the full range of the electron-deficient alkenes that successfully engage in the process, including the breadth of substitution patterns most commonly employed in the additions. Moreover they have thoroughly evaluated the various families of chiral ligands that are effective in promoting high enantioselectivities, including novel classes of phosphorus, sulfur, olefinic, and hybrid ligands. Not surprisingly, given the power of this transformation, applications in the synthesis of natural products abound, and the authors have selected illustrative examples to highlight the utility of the reaction. In one of the most comprehensive treatments, the authors have detailed the use of other classes of organometallic reagents that are susceptible to catalysis by rhodium as well as other transition-metal catalyzed additions of organoboron reagents. Together with ten detailed experimental procedures, this chapter constitutes a dream field guide for the user to identify the best method applicable to solve their particular challenge.

The Tabular Survey comprises 25 tables organized by both substrate structure and organoboron reagent with such a fine granularity as to facilitate with ease the identification of product types sought by those interested in using these methods.

Volume 93 represents the fourteenth single chapter volume to be produced in our 76-year history (seventh in the past fourteen volumes!). Such single-chapter volumes represent definitive treatises on extremely important chemical transformations. The organic chemistry community owes an enormous debt of gratitude to the authors of such chapters for the generous contribution of their time, effort, and insights on reactions that we clearly value.

It is appropriate here to acknowledge the expert assistance of the entire editorial board, in particular Tomislav Rovis and Gary Molander who shepherded this chapter to completion. The contributions of the author, editors, and the publisher were expertly coordinated by the board secretary, Robert M. Coates. In addition, the *Organic Reactions* enterprise could not maintain the quality of production without the dedicated efforts of its editorial staff, Dr. Danielle Soenen, Dr. Linda S. Press, Dr. Dena Lindsey, and Dr. Landy Blasdel. Insofar as the essence of *Organic Reactions* chapters resides in the massive tables of examples, the authors' and editorial coordinators' painstaking efforts are highly prized.

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