PREFACE TO VOLUME 119

What we call the beginning is often the end
And to make an end is to make a beginning.
The end is where we start from.

T. S. Eliot
Little Gidding

Chemists through their ingenuity can develop a variety of methods to achieve similar synthetic goals. Although there are myriad pathways for chemical transformations, these reactions can be reduced to relatively few fundamental types. As Eliot reflects, there are many paths that lead to the same essential truths. The reactions described in the chapters in this volume may seem unrelated at first glance, yet both involve aromatic substitutions. The first chapter reviews the Smiles–Truce rearrangement, the transfer of an aryl group from a heteroatom to a carbanion or carbon-centered radical species. The second chapter covers the Chan–Lam coupling, the oxidative substitution of a heteroatomic nucleophile at a carbon-boron bond in the presence of a copper catalyst or mediator. In the Smiles–Truce rearrangement a carbon-heteroatom bond is broken to form a new carbon-carbon bond, whereas the Chan–Lam coupling forms a new carbon-heteroatom bond by displacement of boron. Thus, the product of the Chan–Lam coupling is the starting material for the Smiles–Truce rearrangement.

Chapter 1 by Effrey A. Noten, Anthony R. Allen, and Corey R. J. Stephenson reviews the Smiles–Truce rearrangement, the intramolecular nucleophilic transfer of an aryl group from a heteroatom to a proximal carbanion or carbon radical. The related Smiles rearrangement, the transfer of an aryl group from one heteroatom to another, was covered in Volume 18 of this series by Truce. The synthetically powerful Smiles–Truce rearrangement allows the conversion of a weaker, relatively easily formed carbon-heteroatom bond to a stronger, often harder to form, carbon-carbon bond, which often significantly simplifies routes to carbon-carbon bond formation in complex target synthesis.

The Mechanism and Stereochemistry section outlines the major mechanistic pathways for both the traditional anionic and the more recent radical Smiles–Truce rearrangement. Intramolecular addition of a carbanion or carbon-centered radical to the *ipso*-carbon of the aryl ring gives an anionic or radical Meisenheimer complex. Subsequent cleavage of the aryl-heteroatom bond restores aromaticity affording the substitution product. Factors controlling the stereoselectivity of Smiles–Truce rearrangements of chiral substrates are described in this section.

The Scope and Limitations section is organized first by the type of heteroatom leaving group. These sections on migration from nitrogen, oxygen, sulfur, and other heteroatoms are then further arranged by the type of reactive carbon species (e.g., alkyl vs. aryl). The Applications to Synthesis section highlights several

examples of pharmaceutical and natural product syntheses where a Smiles–Truce rearrangement was used as a key step to form a challenging carbon-carbon bond. Comparison with Other Methods highlights routes to biaryl compounds by traditional cross-coupling reactions of aryl halides and aryl nucleophiles as well as palladium-catalyzed C-H arylations that give similar products to those obtained in the Smiles–Truce Rearrangement. This section also describes alternate routes to oxindoles, which can be prepared by radical Smiles–Truce rearrangements of *N*-alkyl-*N*-sulfonyl acrylamides, including Friedel-Crafts type reaction with α-halo acetanilides and intramolecular Heck coupling reactions of *N*-aryl amides.

The Tables are organized first by the type of atom from which the aryl group is migrating, including tables focused on aryl migration from nitrogen, oxygen, sulfur, silicon, phosphorus, and selenium and tin. The Tables on aryl migration from nitrogen, oxygen, and sulfur are further divided into sub-tables with examples involving single component reactions and two component reactions in which the Smiles–Truce substrate is formed from two or more reaction partners and then spontaneously undergoes the rearrangement. This chapter provides a critical review of this synthetically powerful method for carbon-carbon bond formation.

Chapter 2 of this volume by John M. Halford-McGuff and Allan J. B. Watson reviews the Chan–Lam coupling, the copper-mediated or -catalyzed oxidative coupling of heteroatom nucleophiles with organoboron compounds. The Chan–Lam coupling proceeds under mild reaction conditions, uses inexpensive copper catalysts or mediators, and has broad substrate scope that makes this reaction complementary to other widely used catalytic carbon-heteroatom bond-forming reactions such as the widely used palladium- or copper-catalyzed coupling of aryl (pseudo)halide electrophiles with heteroatom nucleophiles.

The Mechanism, Chemoselectivity, and Stereoselectivity section describes the current understanding of the mechanism for this transformation using three well-studied systems. The generally understood steps are transmetallation of the organoboron reagent with a copper(II) species followed by oxidation and incorporation of the heteronucleophile to give a copper(III) species that undergoes reductive elimination to the coupled product. In catalytic reactions, the copper(I) species generated upon reductive elimination is oxidized to copper(II) to turn over the catalytic cycle. This section outlines the factors that control the chemoselective arylation of substrates with multiple heteroatom reaction sites and the unresolved challenge of chemoselective reaction of heteronucleophiles with substrates having more than one organoboron moiety. Although stereoselective Chan–Lam couplings are rare, two examples of atroposelective versions are highlighted in this section.

The Scope and Limitations section discusses both components of the Chan–Lam coupling: the organoboron compound and the heteroatom coupling partner. The organoboron section outlines the use of boronic acids, boroxines, boronate esters, and boronates as coupling partners. The section on heteroatom coupling partners covers different classes of nitrogen, oxygen, and sulfur reagents used in the Chan–Lam coupling. Applications of the Chan–Lam coupling in cascade processes are also included. The Application to Synthesis section highlights examples of the Chan–Lam coupling applied in medicinal chemistry and natural product

synthesis. The Comparison with Other Methods section describes other routes to carbon-nitrogen bond formation. The two main classes of reactions discussed are addition of organometallic reagents to nitrogen electrophiles and metal-catalyzed coupling of organic (pseudo)halide electrophiles with heteroatom nucleophiles.

The Tables presents a comprehensive survey of examples in the literature. The primary rubric for table organization is the identity of the heteroatom involved in the coupling in the order nitrogen, oxygen, sulfur, and selenium. The organization is further divided by the class of heteroatom. For example, the nitrogen tables are further broken into various classes of amines, nitrogen heterocycles, and other classes of nitrogen nucleophiles. This chapter provides a comprehensive and critical review of an important route to C-N bond formation.

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