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Book Review

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The Claisen Rearrangement: Methods and Applications

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The [3,3]-sigmatropic rearrangement of allyl vinyl ethers was first reported by Ludwig Claisen in 1912. Since then a number of variants of the Claisen rearrangement have been developed and have found widespread application as a powerful tool for stereocontrolled C-C bond formation in the synthesis of natural products and medicinally important compounds. This book edited by Martin Hiersemann and Udo Nubbemeyer, provides a wide-ranging guide of the different types of Claisen rearrangements and their application in organic synthesis. The book is made up of 11 chapters, with diverse topics ranging from the chorismate-mutase-catalysed Claisen rearrangement through the different variants to a chapter on the mechanistic aspects of the aliphatic Claisen rearrangement. Each chapter varies in length and style ranging from broad overviews of a particular variant of the Claisen rearrangement to specialist reviews of some mechanistic aspect of the Claisen rearrangement.

Chapter 1 outlines the experimental and theoretical investigations of the chorismate-mutase-catalysed Claisen rearrangement and what factors are necessary for this enzyme-catalysed transformation of chorismate to prephenate. In chapter 2, Mikami and Akiyama discuss a chiral variant of the Claisen rearrangement and how different chiral metal complexes such as aluminium(III), copper(II) and palladium(II) can promote the reaction. In chapter 3, Ichikawa and Maruoka then give an excellent overview of most of the general aspects of aliphatic and aromatic Claisen rearrangements discussing the different types of substrates, reaction conditions, transition states and also how the Claisen rearrangement can be included in tandem processes. Chapters 4–10 then detail the different variants of the Claisen rearrangement namely, the Ireland-Claisen rearrangement (Chapter 4),

simple and chelate enolate Claisen rearrangements (Chapter 5), the Claisen-Johnson orthoester rearrangement (Chapter 6), the Meerwein-Eschenmoser-Claisen rearrangement (Chapter 7), the Carroll rearrangement (Chapter 8), the thio-Claisen rearrangement (Chapter 9) and the aza-Claisen rearrangement (Chapter 10). Each of these chapters outlines how these different reactions were discovered and introduces the general substrates and mechanisms of these processes. Each chapter then outlines where appropriate, how studies have led to greater understanding of the regiochemical and stereochemical outcome of these reactions and how this information has been used in the total synthesis of natural products. For example, chapter 6 shows how the Claisen-Johnson orthoester rearrangement can be used as the key step in the total synthesis of indole alkaloids such as tabersonine, ellipticine and tetrahydroalstonine, while chapter 8 describes the application of the Carroll rearrangement for the synthesis of natural products such as isocomene and the antibiotic, acetomycin. Chapters 4–9 are clearly written with good examples and a variety of different applications. Chapter 10, while instructive, could have included more than a passing mention of the Overman rearrangement, a variant of the aza-Claisen rearrangement, widely used in organic synthesis. The final chapter by Rehbein and Hiersemann, then describes in detail the mechanistic aspects of the aliphatic Claisen rearrangement, outlining factors that affect the rates such as substituents and solvents, and how computational studies can help predict the likely transition states of these processes.

In conclusion, this book is a timely, important addition to the area of pericyclic reactions, giving a reasonably thorough overview of the different variants of the Claisen rearrangement and its application in organic synthesis. As this book covers the major aspects of this rearrangement reaction in good detail it will provide a useful reference for postgraduates and researchers working in the field of pericyclic reactions.

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