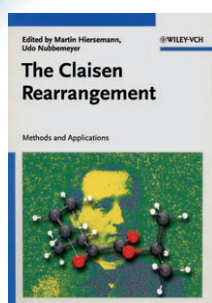




The Claisen Rearrangement



Methods and Applications.
Edited by *Martin Hiersemann* and
Udo Hubbemeyer.
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The Claisen Rearrangement is the first monograph devoted to this elegant C–C coupling reaction, which was originally reported by Ludwig Claisen in 1912. First of all, it should be noted that this book fulfills its purpose of describing and explaining the methods and applications of the Claisen rearrangement, in that it not only contains results from the editors Martin Hiersemann and Udo Hubbemeyer, but also includes contributions from more than 20 scientists throughout Europe, the United States, Japan, and India. Although a number of review articles about [3,3] sigmatropic rearrangements have been published during the last three decades, this book provides in 11 chapters a considerably deeper insight into the Claisen rearrangement, including all its variants. Furthermore, it focuses particularly on new developments, without neglecting theoretical basics and mechanistic aspects. Stereochemical outcomes of many reactions are discussed in detail. The table of contents is clearly laid out, thereby allowing fast access to specific topics.

In view of the enormous importance of the Claisen rearrangement in microorganisms and plants, the editors devote the first chapter entirely to the enzyme

chorismate mutase, which catalyzes the pericyclic transformation of chorismate into prephenate, as one of the key steps in the biosynthesis of aromatic amino acids. The detailed and graphic description of substrate binding within the active site and the discussion of the catalytic mechanisms convey an exciting insight into a rather exotic process in nature.

The second chapter gives an overview of the most important metal centers—aluminum, copper, and palladium—in chiral Lewis acids that are capable of accelerating the rearrangement process. The interesting mechanistic considerations in the examples that are described underscore the importance of the modern catalytic possibilities of the Claisen rearrangement, which was formerly usually carried out as a thermal reaction. While it is of general interest, this chapter will primarily serve the organic chemist who is seeking a suitable catalyst for his or her own “Claisen problem”.

The third chapter, which deals with the aliphatic Claisen rearrangement, also reviews the various approaches to the synthesis of substrates that contain an allyl vinyl ether substructure, in consideration of the fact that the synthesis of these compounds is often considerably more challenging than the rearrangement process itself. The chapter discusses rearrangements of cyclic substrates, tandem reactions, and carbocation-stabilized processes, and also gives an in-depth review of all the facets of the aromatic Claisen rearrangement.

In later chapters, the book focuses on the variants of the Claisen rearrangement, such as the Johnson and Eschenmoser reactions, and in particular the Ireland–Claisen reaction. In view of the great importance of the latter reaction, which was applied, for example, in the synthesis of the prostanoid skeleton and the complex spiroketal monensin, numerous applications in natural product syntheses are presented.

Following a chapter dealing with the Carroll reaction, which has gained importance in the commercial production of carotinoids, two further chapters discuss the rarely encountered hetero-Claisen reactions, in which the allyl vinyl ether oxygen atom is replaced by either

sulfur or nitrogen atoms. In view of their minor importance, a shorter summary of these reactions would probably have sufficed.

On the other hand, special emphasis must be given to the final chapter, which covers the mechanistic aspects of the aliphatic Claisen rearrangement, thereby providing a worthwhile summary—particularly for students—of current knowledge about the reaction process.

In view of the vast number of examples that are described, it appears somewhat disappointing that a couple of new developments and applications in recent years have been disregarded. The literature coverage hardly extends beyond 2004. For example, the book does not mention any of the interesting ring enlargements of carbohydrate derivatives to give highly functionalized carbocycles. Also, although there is a detailed description of organoaluminum compounds as catalysts, the reader does not find any reference to the efficient promoters triisobutylaluminum and diisobutylaluminum hydride.

Considered as a whole, *The Claisen Rearrangement* can be recommended to every synthetic chemist dealing with [3,3] sigmatropic rearrangements, whether in academia or industry. Some chapters are suitable as material to prepare for examinations. After nearly a century since the discovery of the Claisen rearrangement, this monograph provides a detailed and comprehensive overview of an important reaction in organic chemistry.

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