

Preface

Historically, the thermal rearrangement of aromatic and aliphatic allyl vinyl ether was first published in 1912 by Ludwig Claisen. The neat carbon variant of this 3,3 sigmatropic bond reorganization, the Cope rearrangement, was reported in 1940, 38 years later. Thus, the Cope reaction should have been termed as a 3-carba-Claisen rearrangement. However, the reverse is found within the literature: the Claisen rearrangement is termed as a 3-oxa-Cope rearrangement. Consequently, the hetero Claisen reactions are found as 3-hetero-Cope conversions displaying heteroatoms such as nitrogen and sulfur in position 3 of the rearrangement framework. Carrying out a keyword supported literature search, this inconsistent use of synonyms describing one and the same process should be strongly considered. Within our book, we will use the historically exact name *Claisen* rearrangement. Considering the widespread applications of the Claisen rearrangement, we should keep in mind that Mother Nature has been utilizing the aliphatic version already for a much longer period of time: the enzyme-catalyzed rearrangement of chorismate into prephenate also follows the same mechanism.

Although nowadays almost anybody seems to know something about the Claisen rearrangement, the exact nature of the transition state and the way substituents and solvents influence the rate and the selectivity of the reaction can be very difficult to elucidate. However, for the vast majority of applications, qualitative guidelines are sufficient to predict and/or explain the course of a Claisen rearrangement. One of the main conclusions from this book is that there isn't *the* Claisen rearrangement but a truly amazing number of mechanistically related variations of it that have been and are being developed. In this context, the first *Claisen book* presents a platform concerning basics and the state of the art.

From the breathtaking number of applications in target-oriented synthesis it becomes evident that the Claisen rearrangement (and its variants) is one of the most powerful stereoselective carbon-carbon-bond forming reactions. The efficiency of the reaction clearly profits from its atom economy. However, to be honest, access to the actual substrate for the rearrangement may prove costly. A particular strength is the predictability of the stereochemical course of the rearrangement based on the knowledge of the geometry of the cyclic transition state.

Still, even after more than 90 years of development, optimization and application of Claisen rearrangements, there is still plenty of room for further research.

With this in mind, we intended to provide interested researchers with a useful guide to the scope and limitations of this versatile rearrangement. To realize this task, we had to rely on various specialists who were originally contacted in the beginning of 2003 and, indeed, many of them agreed to contribute to the *Claisen book*. We are deeply indebted to all the authors who spent their limited time resources to compile a truly outstanding collection of facts concerning the various Claisen rearrangements. This book will certainly serve as a reference for many years to come.

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