

Studies in Natural Products Chemistry: Chapter 3. Synthesis of Bioactive Natural Products by Propargylic Carboxylic Ester Rearrangements

Shazia Anjum, Elena Soriano, José Luis Marco-Contelles



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Studies in Natural Products Chemistry: Chapter 3. Synthesis of Bioactive Natural Products by Propargylic Carboxylic Ester Rearrangements Shazia Anjum, Elena Soriano, José Luis Marco-Contelles Molecular rearrangements occupy center stage in the development of organic synthesis and, consequently, in the impressive achievements that have resulted in the total synthesis of many complex natural products in the last decades. The purpose of this chapter, in this volume of a book series dedicated to the Studies in Natural Product Chemistry, is to show a set of selected and organized molecular rearrangements based on a personal choice of expertise related to the synthesis of complex bioactive molecules. Our selection addresses [3,3]signatropic rearrangements, which continue to provide excellent opportunities for reaching high chemical diversity, operating in efficient synthetic schemes. [3,3]-Sigmatropic rearrangements, such as the Cope and Claisen rearrangements, are among the most basic and useful transformations in synthetic organic chemistry. This is possibly due to the fact that these rearrangements are efficient methods for the synthesis of quaternary, sterically hindered chiral centers, and for the stereoselective formation of carbon-carbon and carbon-heteroatom bonds. In addition, [3,3]-signatropic rearrangements can be easily integrated in, and adapted to, cascade processes as a simple method to prepare complex molecules in atom-efficient reactions. Consequently, in the context of [3,3]-signatropic rearrangements, we focus on the transformations of propargylic esters, whose rearrangements, in different experimental conditions, have been largely exploited for the synthesis of interesting key and useful intermediates. The rearrangements can be promoted by protic acids, Lewis acids, and noble metals such as Pt, Au, or Cu salts, or complexes that have recently emerged as the most popular and potent electrophilic activators of alkynes toward a number of nucleophilic agents, under homogeneous conditions.

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