Domino and Intramolecular Rearrangement Reactions as Advanced Synthetic Methods in Glycosciences

Domino and Intramolecular Rearrangement Reactions as Advanced Synthetic Methods in Glycosciences is an extensive collection of novel methods for both rapidly and atom economically modifying carbohydrates. The book draws together recent research from thirty-five contributors from around the world on the topic. The book broadly categorizes their approaches by two themes: domino and intramolecular rearrangements. The chapters are written from the perspective of organic chemists and emphasize experimental conditions, reaction mechanisms, representative yields, and are accompanied by abundant referencing to published examples where further experimental details can be found.

Carbohydrates are a major class of biomolecules found in eukaryotic and prokaryotic cells. They are encountered as energy storing polymers, or found as glycoconjugates making up components of nucleic acids, and as information rich protein- and lipid-conjugates responsible for mediating intercellular interactions. Glycoconjugates are often identified as mediators of host–pathogen interactions, as immune modulators in bacterial and viral infections, and even as markers for diseases such as cancer. The modification of carbohydrates within the glycoconjugate has become increasingly important for the creation of tools compounds to enable functional studies of these entities in a biological context. The Foreword, written by Samuel J. Danishefsky, a pioneer in organic and oligosaccharide synthesis, frames the importance of carbohydrate modification in glycoconjugates. He states that to enable this study requires chemistry with a high level of regio- and stereocontrol and that "the combination of domino/cascade/rearrangement reactions has become a very powerful tool" for enabling the synthesis of enantiomerically pure intermediates. The Preface reinforces this notion by giving specific reference to the use of chemistry that utilizes carbohydrate building blocks which has led to "revolutionary discoveries in glycobiology, medicinal chemistry, pharmacology, molecular biology and medicine."

The book begins with Pellissier laying out the definition of a domino reaction as defined by Tietze and describes cascade or tandem reactions. Chapter 1 provides a number of examples on the use of carbohydrates as chiral building blocks to afford stereocontrolled domino reactions. Examples involving Hantzsch, Mannich, Ugi, Passerini, Biginelli, Reformatsky-type, and Petasis/Diels–Alder reactions are provided.

The second chapter, by Voigt and Mahrwald, reviews organocatalyzed cascade reactions to produce chain-elongated carbohydrates and primarily focusses on C-glycosides with emphasis on amine-catalyzed decarboxylative Aldol/oxa-Michael cascade reactions employing unprotected saccharides.

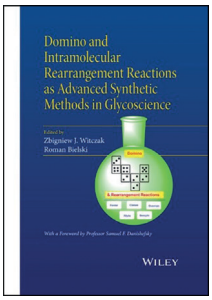
Chapter 3, by Soengas et al., describes metal-promoted reductive ring-opening in domino reactions of carbohydrates. The chemistry focuses on oxidative addition of a metal to an electrophilic site followed by reductive elimination to the open-chain sugar. The subsequent reaction proceeded as a result of this intermediate. The chapter covers examples of the Bernet–Vasella reaction combined with reductive aminations, Barbier-type alkylations, olefinations, and SmI_2-mediated radical cyclization as well as related reactions.

Cachatra and Rauter explore the applications of domino reactions on carbohydrate frameworks in Chapter 4. Several examples of furanose transformations to butenolides, dihydropyridinones, and oxetanes are provided. The chapter also covers selected examples of the conversion of pyranoses to bislactones and deoxysugars.

Chapter 5, by D'Alonzo et al., reviews the use of bis-thioenol ethers as allylic alcohol or β-acyl vinyl anion equivalents. The chapter then turns its attention to the use of these functionalities for the de novo synthesis of carbohydrates. The chapter presents an alternative to the more common approach of refunctionalization of naturally occurring carbohydrate feedstocks and covers selected examples of the synthesis of hexoses, 4-deoxyhexoses, and 4'-substituted nucleosides.

In Chapter 6, Witczak and Bielski review thioclick reactions on levoglucosenone as well as domino reactions as a means of modifying carbohydrates with heterocycles. Selected examples include the use of carbohydrates in azide–olefin [3+2] cycloadditions, copper-catalyzed azide-alkyne cycloadditions, Marckwald syntheses, and several other examples.

Andreana et al. compile an impressive seventy-three page review of the use of isocyanides and their role in multi-component reactions with examples specific to carbohydrates in Chapter 7. The chapter starts with the Passerini and Ugi reactions and thoroughly reviews the use of convertible isocyanides. Numerous examples related to medicinal and natural product chemistry are provided. Many of the examples are accompanied by mechanistic explanations. The chapter concludes with selected applications of glycosides as either glycosyl amines, glycosyl isocyanides, or isocyanoglycosides and their use in these multi-component reactions.



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Chapter 8 by Werz reviews domino reactions yielding annulated carbohydrates at their core. The chapter covers the use endocyclic enol ethers to generate spiroketals and a clever domino carbopalladation approach to preparing various chroman and isochroman derivatives.

Chapter 9 by Witczak and Bielski offers a different perspective on rearrangement reactions applied to carbohydrates. The chapter reviews diverse examples of the Chapman, Hofmann, Cope, Ferrier, Claisen, Overman, and Baeyer–Villiger rearrangements applied to carbohydrate scaffolds.

Jarosz and colleagues describe rearrangements that change the backbone or skeleton of the starting carbohydrate structure in Chapter 10. This is in contrast to reactions that alter the arrangement of substituents on the backbone which are also briefly reviewed. The authors cover selected ring contraction and expansion reactions. Other areas of coverage include rearrangements producing open chain-chain derivatives. One particular example is provided that was described as the inspiration for the "pentenyl glycoside methodology" which evolved to become an important glycosylation method. The remainder of the chapter covers approaches to generating higher carbon sugar derivatives with an emphasis on sugar allyltin reagents.

Chapter 11, by Bielski and Witczak, covers selected chemistry of levoglucosenone which is produced on a large scale from biomass. Levoglucosenone is a versatile chiral synthon which can undergo a variety of transformations. The text provides examples of 1,3-dipolar cycloadditions, Diels-Alder reactions, and participation in Michael additions to name a few.

Marzabadi and co-workers describe "The Preparation and Reactions of 3,6-Anhydro-D-glycals" in Chapter 12. Anhydrosugars often find use for the formation of C–C and C–X bonds. They are useful building blocks in synthesis do to this reactivity. The chapter focuses on the less well-known chemistry of the anydroglycals and reviews the electrophilc and radical-induced additions to these underutilized entities.

Chapter 13, by Jayaraman and co-workers, reviews pyranoside ring expansions to produce septanosides. Diverse approaches to these species are covered including hemiacetal formation, Knoevenagel condensation, Baeyer–Villiger oxidation, ring-closing metathesis and the Nicolas-Ferrier rearrangement. Significant attention is paid to the role of ring expansions utilizing cyclopropane intermediates. The chapter also provides insight into further functionalization and conformational analysis of these unusual saccharides.

Chapter 14, by Herradón and co-workers, describes rearrangements of carbohydrate templates as a pathway to functionalized heterocycles and peptides. They provide examples of peptide-carbohydrate scaffold hybrids, natural products containing both peptide and carbohydrate, and an excellent example of a complex domino reaction involving azide–alkene cycloaddition/nitrogen extrusion/imine-enamine isomerization/nucleophilic addition all applied on a carbohydrate scaffold.

The final Chapter, by Nguyen et al., describes his group's extensive efforts to develop stereoselective nickel-catalyzed glycosylation chemistry. The authors review key examples of naturally occurring glycosides and the application of Pd-catalyzed trichloroacetimidate chemistry in their twenty-five page account paying special attention to stereoselective alpha and beta-linked urea glycoside mimetics.

In summary, this text represents a comprehensive collection of methods and examples of domino reactions applied to the field of carbohydrates. It provides a unique snapshot of the emerging directions in glycosciences from distinguished investigators located around the globe. It provides an indispensable collection of useful reactions and would appeal to medicinal chemists, lecturers seeking to develop a special topics course in the glycosciences, or the investigator striving to stay abreast of current developments in the field.

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