

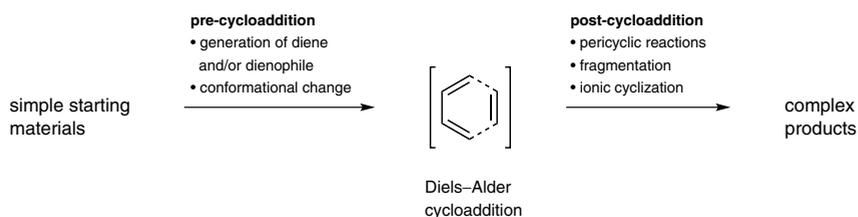
## Abstracts

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### 2.1.1 The Diels–Alder Cycloaddition Reaction in the Context of Domino Processes

*J. G. West and E. J. Sorensen*

The Diels–Alder cycloaddition has been a key component in innumerable, creative domino transformations in organic synthesis. This chapter provides examples of how this [4+2] cycloaddition has been incorporated into the said cascades, with particular attention to its interplay with the other reactions in the sequence. We hope that this review will assist the interested reader to approach the design of novel cascades involving the Diels–Alder reaction.



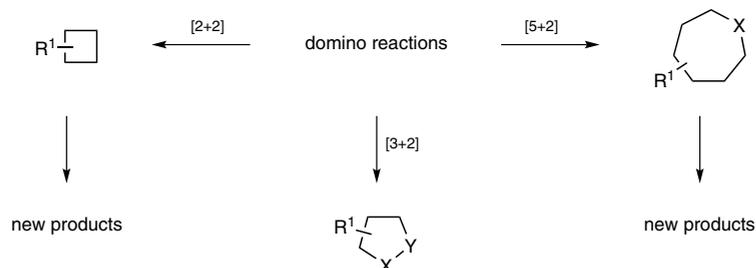
**Keywords:** Diels–Alder · cascade · domino reactions · pericyclic · [4+2] cycloaddition

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### 2.1.2 Domino Reactions Including [2+2], [3+2], or [5+2] Cycloadditions

*I. Coldham and N. S. Sheikh*

This chapter covers examples of domino reactions that include a [2+2]-, [3+2]-, or [5+2]-cycloaddition reaction. The focus is on concerted reactions that occur in a tandem sequence in one pot, rather than overall “formal cycloadditions” or multicomponent couplings. The cycloaddition step typically involves an alkene or alkyne as one of the components in the ring-forming reaction. In addition to the key cycloaddition step, another bond-forming reaction will be involved that can precede or follow the cycloaddition. This other reaction is often an alkylation that generates the substrate for the cycloaddition, or is a ring-opening or rearrangement reaction that occurs after the cycloaddition. As the chemistry involves sequential reactions including at least one ring-forming reaction, unusual molecular structures or compounds that can be difficult to prepare by other means can be obtained. As a result, this strategy has been used for the regio- and stereoselective preparation of a vast array of polycyclic, complex compounds of interest to diverse scientific communities.



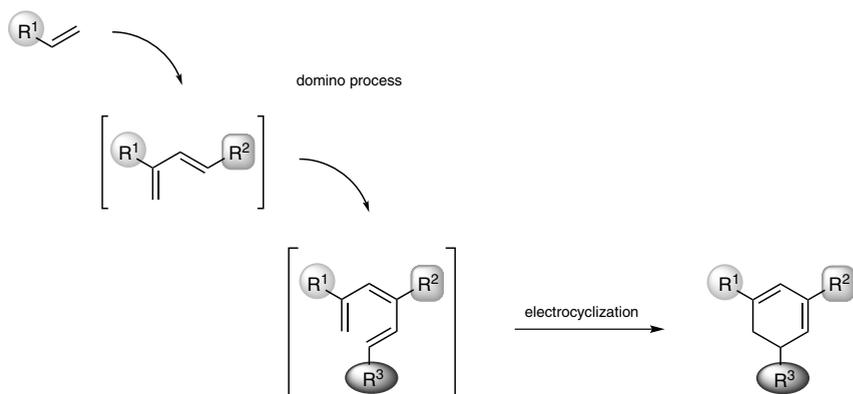
**Keywords:** alkylation · [2+2] cycloaddition · [3+2] cycloaddition · [5+2] cycloaddition · dipolar cycloaddition · domino reactions · Nazarov cyclization · ring formation · [3,3]-sigmatropic rearrangement · tandem reactions

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### 2.1.3 Domino Transformations Involving an Electrocyclization Reaction

*J. Suffert, M. Gulea, G. Blond, and M. Donnard*

Electrocyclization processes represent a powerful and efficient way to produce carbo- or heterocycles stereoselectively. Moreover, when electrocyclizations are involved in domino processes, the overall transformation becomes highly atom and step economic, enabling access to structurally complex molecules. This chapter is devoted to significant contributions published in the last 15 years, focusing on synthetic methodologies using electrocyclization as a key step in a domino process.



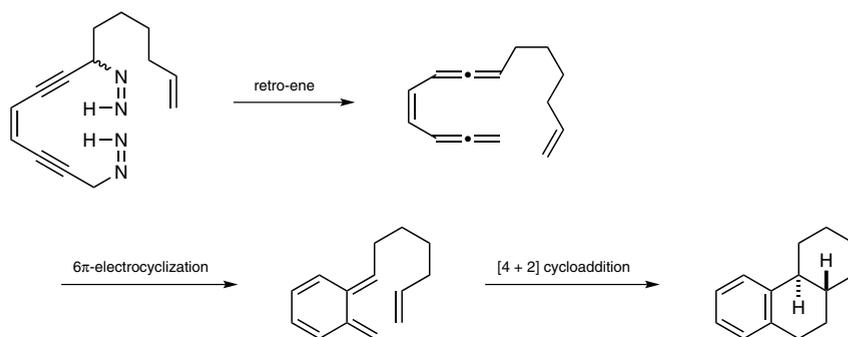
**Keywords:** electrocyclization · hetero-electrocyclization · domino reactions · cascade reactions

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### 2.1.4 Sigmatropic Shifts and Ene Reactions (Excluding [3,3])

*A. V. Novikov and A. Zakarian*

This chapter features a review and discussion of the domino transformations initiated by ene reactions and sigmatropic rearrangements, particularly focusing on [2,3]-sigmatropic shifts, such as Mislow–Evans and Wittig rearrangements, and [1,n] hydrogen shifts. A variety of examples of these domino processes are reviewed, featuring such follow-up processes to the initial reaction as additional ene reactions or sigmatropic shifts, Diels–Alder cycloaddition, [3+2] cycloaddition, electrocyclization, condensation, and radical cyclization. General practical considerations and specific features in the examples of the reported cascade transformation are highlighted. To complete the discussion, uses of these cascade processes in the synthesis of natural products are discussed, demonstrating the rapid assembly of structural complexity that is characteristic of domino processes. Overall, the domino transformations initiated by ene reactions and sigmatropic shifts represent an important subset of domino processes, the study of which is highly valuable for understanding key aspects of chemical reactivity and development of efficient synthetic methods.



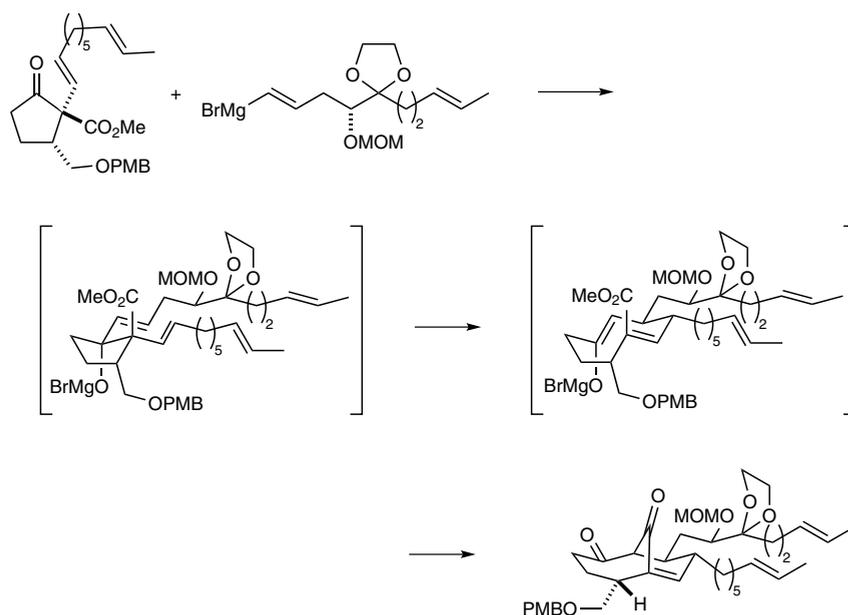
**Keywords:** ene reaction · sigmatropic shift · domino reactions · cascade reactions · hydrogen shift · [1,3]-shift · [1,5]-shift · [1,7]-shift · [2,3]-shift · [3,3]-shift · Mislow–Evans rearrangement · Wittig rearrangement · Diels–Alder cycloaddition · Claisen rearrangement · oxy-Cope rearrangement · electrocyclization · chloropupukeanolide D · isocedrene · steroids · mesembrine · joubertinamine · pinnatoxins · sterpurene · arteannuin M · pseudomonic acid A

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## 2.1.5 Domino Transformations Initiated by or Proceeding Through [3,3]-Sigmatropic Rearrangements

C. A. Guerrero

This chapter concerns itself with domino transformations (i.e., cascade sequences and/or tandem reactions) that are either initiated by or proceed through at least one [3,3]-sigmatropic rearrangement. Excluded from this discussion are domino transformations that end with sigmatropy. The reactions included contain diverse forms of [3,3]-sigmatropic rearrangements and are followed by both polar chemistry or further concerted rearrangement.

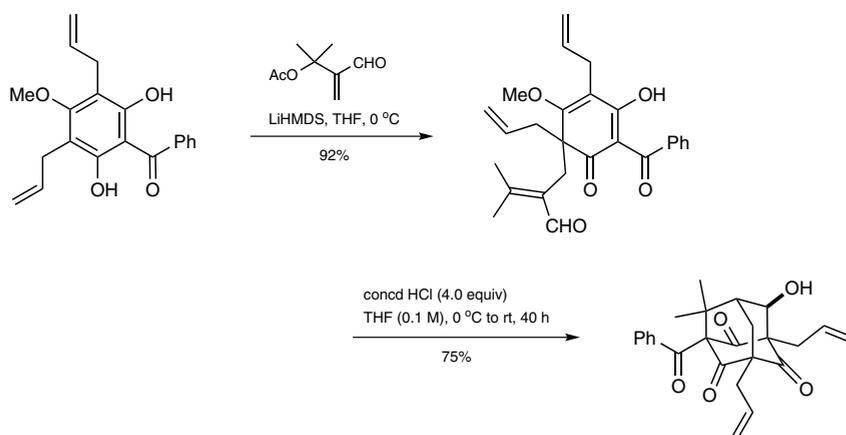


**Keywords:** rearrangement · sigmatropic · Bellus–Claisen · Cope · Overman · concerted · stereoselective · stereospecific · ene · trichloroacetimidate · Diels–Alder

## 2.2 Intermolecular Alkylative Dearomatizations of Phenolic Derivatives in Organic Synthesis

*J. A. Porco, Jr., and J. Boyce*

Intermolecular alkylative dearomatization products have shown promise as synthetic intermediates with diverse capabilities. This chapter describes the available methods for constructing these dearomatized molecules and demonstrates their value as synthetic intermediates for efficient total syntheses.

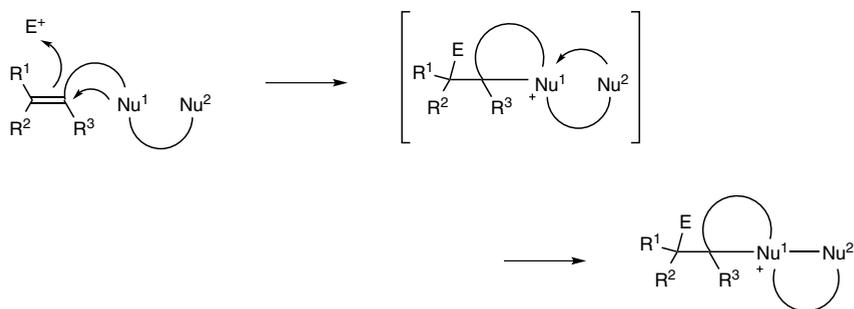


**Keywords:** alkylative dearomatization · dearomative alkylation · dearomative substitution · domino transformations · domino sequences · dearomative domino transformations · cationic cyclization · radical cyclization · alkylative dearomatization/annulation

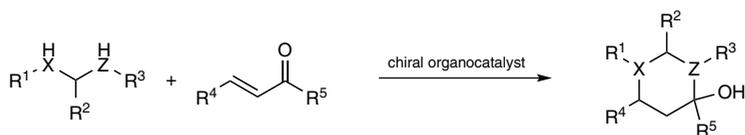
### 2.3.1 Additions to Nonactivated C=C Bonds

*Z. W. Yu and Y.-Y. Yeung*

Electrophilic additions to nonactivated C=C bonds are one of the well-known classical reactions utilized by synthetic chemists as a starting point to construct useful complex organic molecules. This chapter covers a collection of electrophile-initiated domino transformations involving alkenes as the first reaction, followed by reaction with suitable nucleophiles in the succession and termination reactions under identical conditions. The discussion focuses on recent advances in catalysis, strategically designed alkenes, and new electrophilic reagents employed to improve reactivity and control of stereochemistry in the sequence of bond-forming steps.







$R^5 = \text{H}, \text{CO}_2R^6$

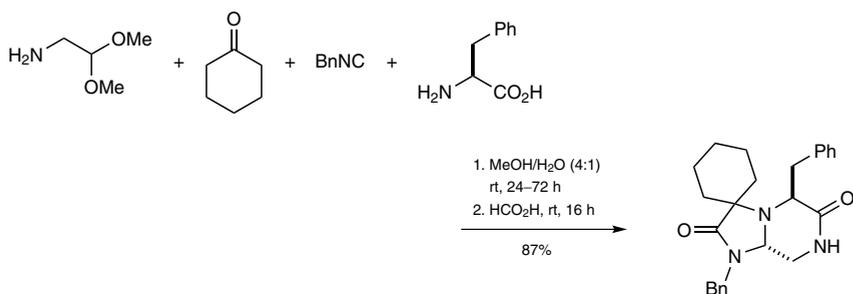
**Keywords:** aldol reactions · carbonyl ylides · chiral amine catalysis · domino reactions · epoxy alcohols · Lewis acid catalysis · Michael addition · organocatalysis · phosphoric acid catalysis · thiourea catalysis

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### 2.3.4 Additions to C=N Bonds and Nitriles

*E. Kroon, T. Zarganes Tzitzikas, C. G. Neochoritis, and A. Dömling*

This chapter describes additions to imines and nitriles and their post-modifications within the context of domino reactions and multicomponent reaction chemistry.



**Keywords:** multicomponent reactions · domino reactions · isocyanides · Ugi reaction · Pictet–Spengler reaction · Gewald reaction · isoindoles · benzodiazepines · cyanoacetamides · thiophenes