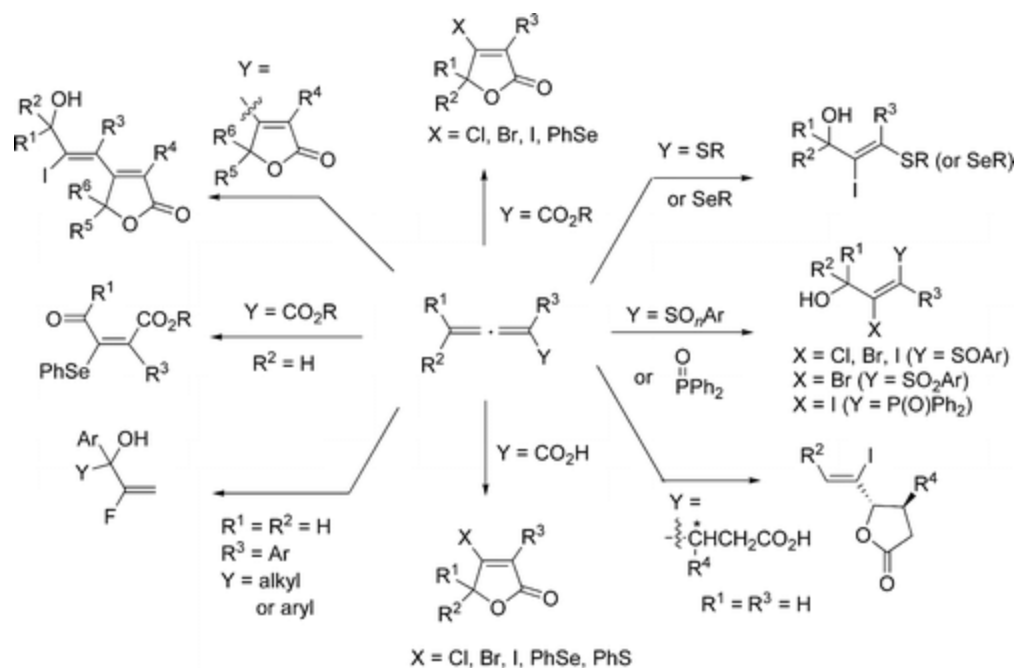


Electrophilic Addition and Cyclization Reactions of Allenes

Shengming Ma *Acc. Chem. Res.*, 2009, 42 (10), pp 1679-1688



Modern organic synthesis depends on the development of highly selective methods for the efficient construction of potentially useful target molecules. A primary goal in our laboratory is the discovery of new reactions that convert readily available starting materials to complex products with complete control of regio- and stereoselectivity. Allenes are one underused moiety in organic synthesis, because these groups are often thought to be highly reactive. However, many compounds containing the allene group, including natural products and pharmaceuticals, are fairly stable. The chemistry of allenes has been shown to have significant potential in organic synthesis.

Electrophilic additions to allenes have often been considered to be synthetically less attractive due to the lack of efficient control of the regio- and stereoselectivity. However, this Account describes electrophilic reactions of allenes with defined regio- and stereoselectivity developed in our laboratory. Many substituted allenes are readily available from propargylic alcohols. Our work has involved an exploration of the reactions of these allenes with many different electrophiles: the *E*- or *Z*-halo- or seleno-hydroxylations of allenyl sulfoxides, sulfones, phosphine oxides, carboxylates, sulfides or selenides, butenolides, and arenes, and the halo- or selenolactonization reactions of allenoic acids and allenoates.

These reactions have produced a host of new compounds such as stereodefined allylic alcohols, ethers, amides, thiiranes, and lactones. In all these reactions, water acts as a reactant and plays an important role in determining the reaction pathway and the stereoselectivity. The differing electronic properties of the two C=C bonds in these allenes determine the regioselectivity of these reactions. Through mechanistic studies of chirality transfer, isolation and reactivity of cyclic intermediates, ¹⁸O-labeling, and substituent effects, we discovered that the *E*-stereoselectivity of some reactions results from the neighboring group participation of functional groups forming cyclic intermediates. We rationalize *Z*-stereoselectivity under other conditions by soft Lewis acid–base interactions and steric effects. These electrophilic reactions

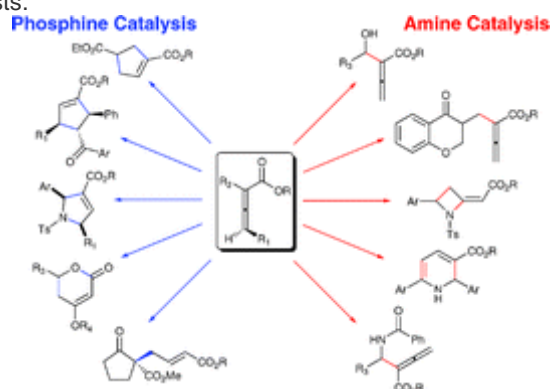
of allenes are efficient and useful methods for the synthesis of stereodefined alkenes and lactones, useful functionalities for synthesis.

Chem. Soc. Rev., 2009, **38**, 3102 - 3116

Enantioselective catalysis and complexity generation from allenoates

Bryan J. Cowen and Scott J. Miller

Lewis base catalysis of reactions with allenoates using phosphine and amine nucleophiles has emerged as a key platform for the generation of molecular complexity. Investigations in this area have established a range of suitable coupling partners for allenoates, including electron-deficient olefins, imines, and aldehydes. This *tutorial review* will describe these methodologies, with a special emphasis on recent work regarding asymmetric reactions using chiral Lewis base catalysts.



Chem. Soc. Rev., 2009, **38**, 2993 - 3009

The art of total synthesis through cascade reactions

K. C. Nicolaou and Jason S. Chen

The growing importance of cascade reactions reflects and imparts advances in the state of the art of organic synthesis and underscores the desire of synthetic chemists to achieve higher levels of elegance and efficiency. Besides their esthetic appeal, cascade processes offer economical and environmentally friendly means for generating molecular complexity. Because of their many advantages, these reactions have found numerous applications in the synthesis of complex molecules, both natural and designed. In this *tutorial review*, we highlight the design and execution of cascade reactions within the context of total synthesis as demonstrated with selected examples from these laboratories.

