

## Book Review

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### Modern Allene Chemistry

Wiley-VCH, 2004, 1143 pp; Price £270.  
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This two-volume set, appearing 20 years after the last monograph on this topic, provides an intensive overview of *Modern Allene Chemistry*. In 20 well-written chapters, nearly all aspects of the fascinating chemistry of cumulated diene systems are considered. Originally regarded as laboratory curiosities, known by many students only as an example of axial chirality, allenes have become increasingly popular in modern organic chemistry. Properties such as being highly energetic compounds (opens the possibility for multistep sequences), their unique stereochemistry and the acidity of the hydrogen atoms have catapulted allene chemistry forward.

The two volumes have been carefully organized. In the first of the 20 chapters, written by Hashmi, prototropic and sigmatropic isomerization reactions to form allenes are discussed. After this kind of warm up, the next chapters deal with more recent synthetic methods, such as metal-mediated (Krause) and metal-catalysed reactions to prepare allenic systems, as well as their enantioselective synthesis. This latter chapter describes methods such as substrate control, reagent control, enantioselective catalysis and recent efforts in kinetic resolution. The next part deals with special classes of allenes, such as allenic hydrocarbons (Hopf), strained allenes (Christl), acceptor-substituted (Banert) and donor-substituted allenes (Reissig). Numerous examples demonstrate how strain, electron-withdrawing effects and electron-releasing effects influence the reactivity of the allenic  $\pi$  system. On the one hand, Michael acceptor-type chemistry is discussed; on the other hand, enol ether or enamine reactivity is observed and a wide range of possible cycloaddition reactions is elucidated. By using these methods, one gains access to a plethora of highly functionalized heterocyclic systems.

The second volume elucidates all facets of the rich reactivity of allenes, as well as

applications such as their use as pharmaceuticals and key intermediates in natural product synthesis. Of course, some aspects already mentioned in the first volume are discussed again, but here they are embedded in a different context. Thus, instead of being a repetition, only the reader's point of view changes. The chapters of this second volume are very different in length. The first chapter provides a very detailed description of ionic reactions (Ma). The importance of more recent reactions is illustrated by free-radical additions, cycloadditions, cyclizations, and oxidations of allenes. All the transition-metal-mediated allene chemistry is discussed in three chapters, written by Reissig, Hashmi and Mandai. These chapters are of special value for the synthetic organic chemist. However, many of these reactions discussed here are not understood in detail, and subtle changes in catalyst or reaction conditions result in a completely different outcome. In my opinion, future research will be focused in this area to get better insights to answer the question 'How does this reaction work?' The three final chapters under the general heading 'Applications' demonstrate that the 'laboratory curiosity' allene has been used by Nature for millions of years. Nowadays, about 150 natural products comprising an allenic or cumulenenic structure are known, many of them isolated from algae and insects. Allenic analogues of steroids and nucleosides have been used as enzyme inhibitors and antiviral agents. One also assumes that the DNA cleavage mechanism initiated by neocarzinostatin is the result of an intermediate allene formation, which subsequently undergoes Myers-Saito cyclization to afford an aromatic biradical. This fascinating radical chemistry of enyne-allenes is highlighted in the very last chapter, showing wonderful reaction cascades affording highly fused polyaromatic structures.

Overall, it was a pleasant experience to read the books. In some chapters a more consecutive numbering of the compounds would have been appropriate and would have significantly improved ease of reading. Some authors abstain from writing a conclusion, which in my opinion is an important (although small) part of a book chapter. Unfortunately,

the extent of cross-references is really too small—the connections between the different topics sometimes remain unclear. I missed a part dealing with physical organic aspects of allenes, such as electronic properties (UV-Vis spectra, photoelectron spectroscopy) and structural investigations—are these topics not modern any more? The nice cover picture showing a blue-coloured poison-dart frog might lead the casual observer to assume that the bromoallene also shown below is a metabolite of this species. In fact, this compound is generated by red algae and the frog is responsible for the synthesis of a different toxic allene.

All chapters, even though they vary greatly in length, are clearly structured and provide a perfect overview of the special topics. Special care has been taken to achieve clarity in drawing and editing of the chemical formulae, reaction schemes, figures, and tables (I could find only a few errors). To complete the picture, there is a detailed list of contents, a long subject index of about 1500 entries—but not all of them are really useful—as well as a tremendous number of literature citations that serve as a guide for the reader and invite for further reading. Despite the high price of £270 (two volumes, 1143 pages in total), I certainly recommend this exciting and rounded opus to all researchers in the field of allene chemistry. Chemists working in hydrocarbon, transition metal chemistry and natural product synthesis could also gain a significant amount of information valuable to their own research. Overall, *Modern Allene Chemistry* provides an excellent snapshot of the state of the art in allene chemistry in 2004, fits perfectly well in the VCH "Modern Chemistry" series, and should not be missing as the new standard work of allenes in any good library collection. Chemists in academia and in industry will benefit from this opus.

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