

Book-reviews

Modern Carbonyl Olefination – Methods and Applications, in: Takeshi Takeda (Ed.), Wiley-VCH, 2004 349 pp, Hardcover, ISBN: 3-527-30634-X.

Reactions in which two halves of a complex molecule are linked by means of a convergent synthetic strategy belong to the most valuable framework-building reactions in organic synthesis. Especially successful are those reactions in which C=C double bonds are formed, such as the Wittig reaction and its variants according to Horner, Wadsworth, and Emons. Decisive for the effectiveness of these methods is the simple preparative access to both individual components: a carbonyl compound as well as a Wittig-type reagent, which can be obtained, for instance, by the reaction of an alkyl halide with phosphanes or phosphites followed by deprotonation. Only such a simple and general approach enables the synthetic chemist to convert any two complex building blocks into carbonyl and Wittig-reagent components in a late step of the synthetic sequence. The components can be subsequently coupled by either an inter- or intramolecular olefination reaction.

However, Wittig-type reactions are also subject to certain limitations. One example is the *cis* selectivity upon use of nonstabilized ylides under salt-free reaction conditions.

Fortunately, the Wittig-type reactions can be supplemented by the Julia-Lythgoe olefination, which is a general method for preparing *trans*-disubstituted olefins.

The components required for the Julia-Lythgoe olefination, the carbonyl and sulfone components, also meet the criterion of being readily available and allow the corresponding functionalization in a late synthetic step.

Another disadvantage of Wittig-type reactions is their limitation to aldehydes and ketones as the carbonyl component; carboxylic acid derivatives are generally inert in this respect. Furthermore, Wittig-type reactions and Julia-Lythgoe olefinations both require a more or less basic reaction medium. Especially in the case of easily enolizable carbonyl compounds, this can lead to undesired side reactions such as elimination and racemization of adjacent stereocenters. The olefination of sterically demanding carbonyl substrates also clearly demonstrates the limitations of the Wittig reaction.

For this reason, considerable efforts have been devoted to finding improved olefination reagents that can overcome these shortcomings of both the Wittig-type reactions and Julia-Lythgoe olefinations. A milestone was already reached in 1978 by Tebbe, who recognized the usefulness of the titanium-aluminum complex for carbonyl methylenations.

These reagents are reactive under neutral to slightly Lewis acidic conditions, which allows easily enolizable carbonyl

compounds to be used in methylenation reactions without competing side reactions. Another advantage is the clean methylenation of carboxylic acid derivatives with formation of, for example, preparatively valuable enol ethers and enamines.

All these aspects and more other such as the Peterson, the Schrock-type metal carbene complexes, the low-valent chromium (Lombardo reagent), zinc (Nysted reagent), or titanium mediated reactions (McMurry) are well and extensively discussed in this text which always emphasizes stereochemistry, reaction mechanisms and synthetic applications.

Finally, the last chapter of the book concerning the “Asymmetric Carbonyl Olefination” is the logic conclusion for these intriguing and continuously in expansion reactions, seldom very important as key intermediate in complex synthesis of natural molecules.

Although there are many papers on this topic, this is the first book that pull them all together in one volume that can become a milestone for organic chemists.

In consideration of the deepened treatment of the themes involved it principally addresses specialists of all those sectors in which the carbonyl olefinations is daily utilized as well as post-graduate students.

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T. Eicher, S. Hauptmann,
The chemistry of heterocycles—structure, reactions,
syntheses, and applications 2nd, completely revised
edition, Wiley-VCH, 2003 556 Seiten, paperback.
ISBN: 3-527-30720-6.

Heterocycles are present in natural as well as in synthetic organic compounds of medicinal interest. Vitamins B1 and B12, the penicillins, the benzodiazepines, and most of the

alkaloids are but a few examples of pharmacologically active heterocyclic molecules. An appreciation of the chemistry of heterocycles is therefore of the essence for any pharmaceutical/medicinal chemist.

Eicher and Hauptmann provide an up to date introduction to the field for the advanced undergraduate and graduate students. The book is well suited to accompany a lecture and/or practical course designed for students with a background in basic organic chemistry as it is given in the numerous general textbook of organic chemistry.

The obvious criterion to group the seemingly unlimited diversity of heterocyclic chemical compounds is by ring size. The authors follow this route to organize their book, starting with the smallest possible ring size of three atoms, up to a ring size of seven atoms. The final chapter gives a cursory overview of rings larger than seven member atoms. Preceding their systematic discussion of the molecular classes of heterocycles the authors have included a most welcome introduction to the bewildering nomenclature. The systematic naming of heterocyclic rings is an aspect that is often totally absent from the standard textbooks, even if they do contain a separate chapter on heterocycle chemistry. For the apprentice set out to dive deeply into this topic it is an essential tool, though, that has to be mastered if one is bound not to lose one's way.

In any given chapter of the book the discussion starts with the simplest compounds containing but one heteroatom and proceed on the basis of increasing numbers of heteroatoms, again following an obvious and sensible rationale. The detailed discussion of a specific heterocycle is subdivided into five categories (structure/physical properties; chemical properties; syntheses; derivatives in a wider sense; uses in organic synthesis), each clearly indicated for easy navigation by users wishing to extract specialized information. According to Dr. Thomas Lazar *"this reiterated scheme of organizing the contents the book is not only useful as an advanced textbook for students but very useful as a reference source for the professional chemist, too"*.

The discussion is at a high to very high level throughout. Prior experience in organic chemistry is therefore essential to make full use of The Chemistry of Heterocycles.

The book is carefully produced to a very high standard. The printing of the text and the numerous chemical formulas is of excellent quality. If there were anything to complain about it would be the paperback binding. It can be expected that the volume will suffer from continued use, particularly the wear and tear of using it in the laboratory. An alternative sturdy hardcover edition would be desirable.

For the students trying to get to grips with the topic sub-chapters contain detailed summaries; for the graduate and the professional each of the six "ring chapters" is comprehensively referenced. For the serious student chapter nine presents a full 143 problems and clues how to solve them. The problems are frequently demanding, challenging the student, often requiring consultation of academic journals for guidance and necessary information.

The Chemistry of Heterocycles is a thorough advanced treatise at the interface of the lecture hall and the research laboratory, cleverly designed and rewarding, with a clear potential of a standard reference source of its field of study.

Basing on a personal thorough evaluation complimented by a Students survey Professor U. Chiacchio, Professor A. Corsaro, Professor A. Rescifina (Department of Organic Chemistry, University of Catania) and Professor A. Santagati (Department of Pharmaceutical Sciences, University of Catania) said *"this book successfully provides comprehensive answers at a level appropriate for undergraduate and advanced students. The text is very informative, presenting many attention-grabbing approaches to the development of topics for both organic and medicinal chemists"*.

Salvatore Guccione

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