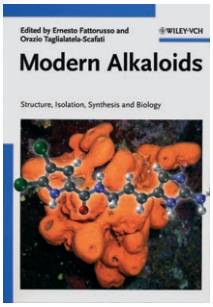
Modern Alkaloids



Structure, Isolation, Synthesis and Biology. Edited by *Ernesto Fattorusso* and *Orazio Taglialatela-Scafati*. Wiley-VCH, Weinheim 2008. 665 pp., hardcover € 189.00.—ISBN 978-3-527-31521-5

From the beginnings of alkaloid chemistry more than 200 years ago, this important class of natural products has been the subject of extensive research, and thus some of the most prominent representatives of alkaloids already fill entire textbooks. In view of the overwhelming amount of material, this book aims to make a virtue out of necessity, by being restricted at the outset to presenting, in 20 independent chapters, a selection of new insights and developments of alkaloid chemistry under the concise title *Modern Alkaloids*.

The book is divided into three sections. The first section (11 chapters) discusses the structures and bioactivities of selected alkaloids from plant sources, and especially from marine sources. The latter are somewhat neglected in many older books on alkaloids, since marine alkaloids have been investigated extensively only for the last 20 years. The second section, which consists of three chapters, is devoted to new methods for the isolation and structural elucidation of alkaloids, while the third section of the book (6 chapters) deals with the synthesis and biosynthesis of selected classes of alkaloids.

In a nice introductory chapter, the ecological role of alkaloids in the chemical defense of plants against herbivores is described, and their effects on neuronal signal transduction are explained. The chapters on alkaloids with antitumor activity, on the bitter taste of many alkaloids, on glycosidase-inhibiting alkaloids, and on neurotoxic and angiogenesis-inhibiting alkaloids also follow the concept of classifying the alkaloids according to their bioactivity rather than structural classes, as in most earlier books. Consequently, the ecological and medical aspects of many alkaloids are especially emphasized. Unfortunately, however, that concept is not followed consistently throughout the whole section. Instead, the other chapters of the first part discuss selected compound classes, namely capsaicinoids, lamellarins, manzamines, bromopyrroles, and guanidine alkaloids. Moreover, the content of these chapters sometimes goes beyond the description of the respective structures and their activities, thereby anticipating aspects that would have fitted better in the second and third sections of the book. For example, the informative chapter on the manzamines, an important structural class, but one that has only been known for 20 years, deals not only with their activity but with their total synthesis. In view of the huge number of alkaloids now known, it is not surprising that only a selection of them could be covered by this book, thus leaving out, for example, most of the alkaloids from fungi.

The second section of the book, taking the tropane alkaloids as an example, begins by discussing some comparatively new techniques for the isolation of natural products, such as supercritical fluid extraction and solid-phase microextraction, as well as analytical methods such as GC–MS, LC–MS, and capillary electrophoresis. This chapter overlaps with the next one, which is entirely devoted to the analysis of alkaloids by LC–MS and the interpretation of MS/MS and MS^3 spectra. The latter method has recently partially replaced the traditionally important EI–MS technique, in the structural analysis of alkaloids as well as elsewhere. The last chapter on modern analytical methods deals extensively with ^{15}N NMR spectroscopy, a method that was previously rarely used because of its low sensitivity and the low natural abundance of ^{15}N. However, the ability to measure ^{15}N chemical shifts has improved greatly in the last few years through indirect detection by the measurement of ^{1}H-^{15}N heteronuclear multiple bond correlations (HMBCs). This chapter especially, and also the preceding one, offer the reader interested in the analysis of alkaloids a good guide and review with a multitude of examples.

The third part of the book is devoted to the synthesis and biosynthesis of selected alkaloids. Thus, there is a description of how carbazoles can be generated by transition-metal-mediated oxidative cyclization reactions. The next chapter gives an overview of different approaches to the total synthesis of camptothecin, while a chapter on the combinatorial biosynthesis of libraries of alkaloid-like compounds reaches beyond the synthesis of natural products. Unfortunately, the selection of the chapters on synthetic methods appears to be especially arbitrary. Because of the multitude of different structures of alkaloids, it is impossible to present more generally applicable modern synthetic methods for alkaloids in just three chapters, and consequently this part is only a patchwork, although the individual chapters are, in themselves, very informative. The same applies to the last three chapters, which focus on the biosynthesis of alkaloids. However, the chapters on daphniphyllum alkaloids and on halogenated alkaloids deal not only with their biosynthesis but also, to a considerable extent, with their structures and activities. Presumably this shortness of presentation is due to the lack of experimental evidence about biosynthetic mechanisms for many alkaloids, particularly those of marine origin. The final chapter discusses future possibilities for biotechnological production of new "non-natural natural products" that arise from the elucidation of the genes responsible for the biosynthesis of alkaloids.

Unfortunately, the book contains some textual errors, mistakes in the formulas, and inconsistencies. For example, the structure formulas of the madangamines are wrong. Furthermore, it is inconvenient that the structure

drawings are not numbered in all chapters.

Since *Modern Alkaloids* does not aim to teach the basics of important alkaloids, but concentrates on new aspects of alkaloid chemistry, it is not so much intended for students as for researchers working in the field of natural products chemistry, where it closes a gap in the literature. The above criticism about the lack of consistency in the organization of the sections is offset by the richness of the contents and the high quality throughout most chapters, which makes the book a valuable treasure trove, not only for natural products chemists but also for researchers in related disciplines who are interested in new developments in alkaloid chemistry. Therefore, I recommend *Modern Alkaloids* warmly to everybody who is interested in natural products chemistry.

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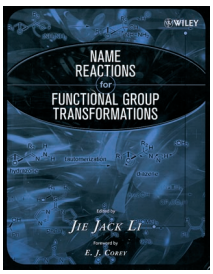
Name Reactions for Functional Group Transformations



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The concept of the functional group has proved to be very useful in organic chemistry as an aid to the planning of syntheses. However, in this enormous and fast-changing field, it is difficult to avoid losing one's overall perspective. E. J. Corey, in his preface to this book, recommends it as a useful work of reference to help overcome that problem. Under the editorship of Jie Jack Li, 19 authors from industry and universities have collected together detailed information about functional-group transformations, categorized in 47 classes. The spectrum ranges from very simple reactions, such as Fischer–Speier esterifications and Zaitsev eliminations, to complex reactions such as Buchwald–Hartwig aminations and Sharpless asymmetric dihydroxylations.

This book is the second volume in the series *Comprehensive Name Reactions*. The first volume, *Name Reactions in Heterocyclic Chemistry*, was published in 2005, and the present one will be followed by three further ones, *Name Reactions for Chain Extension* (2009), *Name Reactions for Ring Formation* (2011), and *Name Reactions in Heterocyclic Chemistry—2* (2013). The complete list of contents of all the volumes is given in the appendix.

The huge flood of information contained in the present volume is brought under control by a clearly set out list of contents and a comprehensive 45-page index. The subject categories are: asymmetric syntheses (5 reactions), reductions (6 reactions), oxidations (13 reactions), olefinations (8 reactions), amine syntheses (3 reactions), syntheses of carboxylic acid derivatives (6 reactions), and a chapter covering various other name reactions (10 reactions). However, the book is not entirely free of errors in the assignment of the reactions to the appropriate chapters: for example, dehydration reactions are not oxidations, but would be better fitted into the chapter on olefinations. Also, some reactions form C–C bonds, and should therefore be grouped with similar reactions in the third volume of the series. On the other hand, some reactions that clearly only involve an interchange of functional groups, such as Sandmeyer and Mitsunobu reactions, have wrongly ended up in Volume 3 of the series.

Throughout this volume there are many useful cross-references to other name reactions. However, the chapter authors seem to have overlooked the fact that the Corey–Kim and Swern oxidation reactions, which are treated in separate chapters, essentially differ only in the reagents whereby the reactive species ("activated DMSO") is generated. Even some of the same literature references are cited. It would certainly have been better to put these reactions in the same chapter, or at least to give cross-references.

As in the first volume of the series, each chapter on a name reaction is consistently divided into the same seven subchapters, which helps one to keep track of the subject matter. First, on the basis of a generalized reaction equation, the characteristics of the reaction are described and briefly explained. That is followed by a historical survey of the discovery and subsequent development of the method. The discussion that follows, about the mechanism of the reaction named in the chapter title, is very detailed in most cases, and often covers many subtle aspects. In contrast, however, in many cases little information is given about the details of other reactions that are mentioned later in the chapter in connection with the title reaction.

The next part of the chapter describes variations in reagents or reaction conditions, which can, for example, give better yields or selectivities, or introduce possibilities of other substrates or transformations, or simply make it easier to perform the reaction. Many of the authors also mention limitations and unwanted side products. This is especially effective and useful in the description of the Fukuyama amine synthesis, where it is given a separate subchapter. Unfortunately, the advantages and disadvantages of the reaction compared with alternative methods for achieving the same transformation are only discussed in a few cases.

In the subchapter entitled "Synthetic Utility", which is usually the longest, readers will find typical applications of the title reaction, perhaps in some cases embedded within a larger synthetic context. Many authors supply this information in a very clear and concise form. However, especially in the chapters on Perkow, Yamada, and Regitz reactions, there are far too many examples of reactions that are very similar (e.g. for the Yamada reaction the chapter lists 78 different amide syntheses covering 37 pages!). These usually do not illustrate any new aspects, but make it difficult to spot the few really interesting variations. It is also hard to understand why some reaction schemes are shown in which the title reaction itself does not play a part, for

