Catalyzed Carbon–Heteroatom Bond Formation

This book edited by Andrei K. Yudin summarizes recent developments in the area of carbon–heteroatom bond formation catalyzed by late transition metals. Covering the range from C–O bonds to C–N, C–S, and the less explored C–Se bonds, the book offers the reader not only a detailed account of the applications of the main players in these transformations (Pd, Rh, Au, etc) but also of the strategies that are available for the synthesis of useful molecular scaffolds. The ability to introduce carbon–heteroatom bonds into organic molecules is of utmost importance: first, C–X functionalities can open up new sites at which molecules can be further modified to introduce molecular complexity; second, the challenges associated with C–X bond formation have stimulated the development of innovative tools for achieving milder and more efficient methods. Finally, C–X bonds are important per se, as most of the key interactions of organic compounds with their biological targets stem from heteroatoms present in the ligand's scaffold. Thus, it is not surprising that the number of publications on C–X bond-forming reactions catalyzed by late transition metals has increased exponentially over the past 15 years.

The book is divided into 12 chapters, each authored by a key expert in the corresponding field. The first chapter, by Wolfe, deals with Pd-catalyzed C–N bond formation to give saturated five-membered rings. In Chapter 2, Dong describes the most recent advances in transition-metal-catalyzed synthesis of lactones, dealing both with mechanistic aspects and with applications to syntheses of highly complex natural products. The third chapter, by Beletskaya, introduces the reader to the area of C_{sp^2}–S and C_{sp^2}–Se bond formation, both via transition-metal-catalyzed cross-couplings as well as by addition-type reactions. The short Chapter 4, by Muñiz, is devoted to the Pd-catalyzed oxidative 1,2-difunctionalization of alkenes. In Chapter 5, Lebel focuses on Rh-catalyzed C–H amination reactions, including some of the more recent stereoselective methods reported up to now. Chapters 6, 8, and 9 deal with syntheses of aromatic heterocycles. The topic has been divided as follows: Pd-catalyzed methods are covered by Arndtsen in Chapter 6, whereas monocyclic and fused five-membered aromatic heterocycles are covered by Gevorgyan in Chapters 8 and 9, respectively. Chapter 7 focuses on the reactions of copper acetylides, especially on catalytic dipolar cycloadditions. In Chapter 10, Lautens reviews the most important contributions on Rh-catalyzed ring opening reactions using oxygen-, nitrogen-, and sulfur-based nucleophiles, with special emphasis on the asymmetric variants of these transformations. The book concludes with two chapters by Widenhoefer on gold catalysis: Chapter 11 deals with N- and S-nucleophile additions to C–C multiple bonds, while Chapter 12 focuses on oxygen nucleophiles.

The chapter organization could be improved. For example, Chapters 6, 8, and 9 seem to belong together, but the first two are separated by Chapter 7, which is completely unrelated. The same could be said of Chapters 5 and 10, both of which deal with Rh-catalyzed processes. More consistency in the length and depth of the chapters would also have been desirable: some chapters are very exhaustive, containing comprehensive tables on the scope of substrates, whereas others have been kept much more "conceptual", just focusing on the strategies and/or mechanisms (which in my view is more appealing for a broader audience). Although there are some noticeable examples of duplication, especially in the case of gold-catalyzed processes, the overlap among the different chapters has been kept to a minimum.

Overall, the book represents a comprehensive reference source, not only for those interested in reading about the latest results on catalytic transformations to form C–heteroatom bonds, but also for those seeking efficient methods to access synthetically relevant organic species such as piperidines, pyrroles, indoles, furans, etc. The individual chapters contain enough background information and up-to-date literature coverage to ensure that the book will continue to be useful over a reasonable period of time in this vibrant field. Every institution concerned with synthetic organic chemistry should have this book available on its shelves.

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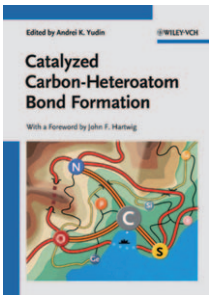

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Image and Reality

Before spectroscopic and other physical methods revolutionized chemistry essentially only two physical tools were available to chemists—most especially to those of the 19th century: the thermometer and the balance. Whereas the first was necessary for the determination of the purity of a substance (through its melting point and/or boiling point), the second served to determine the quantitative composition of compounds. With this

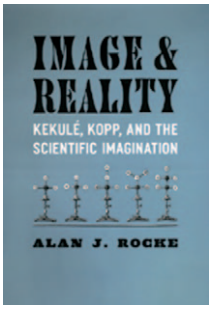

Image and Reality
Kekulé, Kopp, and the Scientific Imagination. Von Alan J. Rocke. The University of Chicago Press, Chicago 2010. 416 pp., hardcover, 45.00 €.—ISBN 978-0226723327

it was indeed possible to determine the type and amount of the elements from which more complex compounds were formed, but nothing about how these building blocks were interconnected in the original substance. More was necessary for the determination of molecular structure, namely a theoretical concept of that which we now call valency, bonding or also structural formula.

How this structural science was arrived at, who were the most important protagonists and how these were "networked" with one another is described by Alan Rocke in his new book. Rocke, Professor for the History of Science at Case Western Reserve University has long been recognized as one of the best authorities on the (organic) chemistry of the 19th century and in addition to numerous journal contributions has already published important monographs, including amongst others on Kolbe (*The Quiet Revolution*, 1993) and Adolphe Wurtz (*Nationalizing Science*, 2001), two researchers, who also play an important role in the current volume.

Image and Reality is not only thoroughly entertainingly and fascinatingly written, but also shows how "modern" the time between 1850 and 1870 already was, when organic structural science was formulated. Almost all protagonists, whether in France (Dumas, Wurtz, Laurent, Gerhardt i.a.), Germany (Liebig, Wöhler, Kolbe, Kekulé, Kopp, Erlenmeyer, etc.), England and Scotland (Frankland, Couper, Brown, Williamson), Russia (Butlerow, Beilstein) or the Netherlands (van't Hoff) not only knew each other personally, but had, for example, studied both under and with one another, visited each other frequently and were in extremely lively scientific contact, even in today's point of view a highly modern and effective scientific organization—only without the web.

The pivotal breakthrough in the understanding of the structure of organic molecules lies in the opinion of the author in the envisagement of mental pictures of the observed chemical transformation. If until then the chemical metamorphosis (Kekulé) took place solely in the flask the actual act of conversion now began in the head, i.e. in the imagination of the scientist, by the formation and modification of pictorial metaphors. In the end the chemical compounds undergoing change behaved in the reaction vessel exactly as had been imagined conceptually, indeed the mind had become the chemical apparatus. These "molecular worlds" (an expression and a writing of Hermann Kopp) were increasingly supplemented by "paper tools", namely the structural formula that became ever increasingly similar to our current structural notation, and by the first molecular models (those of van't Hoff or Kekulé have survived up to today). Chemistry, until then a strictly empirical science, gained through this transformation a more speculative element which was attacked fervently, with powerful eloquence, and even at times offensively by Kolbe, an exponent of classical materialistic chemistry, especially in the case of the new structuralists such as Kekulé and van't Hoff.

The author has successfully achieved the difficult balance of tracing both the broad picture of this international transformation process characterized by a high dynamic as well as the accurately detailed highlighting and description of the contributions of individual protagonists. Of these Kekulé stands out, and even though much biographical material on him exists, Rocke has succeeded in observing and illuminating this certainly most important representative and founder of the new structural science from many different perspectives, be it in tracing the foundation of the actual structural science (key words: tetravalent carbon and "sausage formula"), in discussing the by now proverbial dreams of Kekulé and describing the final act of his life which peaked in the legendary benzene festival in Berlin in 1890. Whether the dreams and stories of Kekulé are anecdotal or "actually" happened is of secondary importance here: they are also metonymic with a new thinking in chemistry, with a conceptualization in metaphor and picture, a chemistry of "as if", which has remained with us until this day for it is easy to learn and is of high heuristic value.

One of the main problems of the developing structural science were the unsaturated or carbon rich compounds and most especially the structure of benzene. Rocke also describes in numerous ramifications the history of this symbolic and fateful molecule of organic chemistry (up to the topical issue of a few years ago whether Kekulé had forerunners who preceded him in the establishment of the hexagonal ring structure). It is therefore especially pleasing that the frontispiece pages and the pages concluding the total text are totally black and have a graphene structure: a paper tool that would certainly have pleased Kekulé.

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