

Book Reviews

Diazo Chemistry I. Aromatic and Heteroaromatic Compounds. By H. Zollinger. VCH: Weinheim, 1994, 453 pp., hardback. DM 198. ISBN 3-527-29213-6.

A comprehensive coverage in a mere reference book was not the purpose of this work, in spite of the inclusion of nearly 2000 references, but rather a critical evaluation and interpretation of a great deal of experimental and theoretical data from an author who, already 33 years ago, had written a fundamental monograph on this matter: "Diazo and Azo Chemistry; Aliphatic and Aromatic Compounds" (1961).

The book is divided in thirteen chapters, each of which has several subsections, a listing of literature references, referred to in the text by the first author and the year of publication, and a subject index.

A short introduction, Chapter 1, deals with historical developments, the general references and the nomenclature. Chapter 2 covers the main methods of synthesis and isolation of aromatic diazo compounds. In Chapter 3 a most excellent account of kinetics and mechanisms of diazotization is set out. Chapter 4 describes the structures of the arenediazonium salts, mainly by X-ray analysis and ^1H , ^{13}C and ^{15}N -NMR, and to a minor extent by IR, UV and mass spectrometry, and theoretical investigations concerning structures, electronic spectra and reactivity. The following three Chapters, 5, 6 and 7, cover a wide range of topics in the addition of nucleophiles to arenediazonium ions, considered as Lewis acids, including the acid-base equilibria in aqueous solution and the mechanistic aspects. Chapter 8 deals with one of the most intriguing aspects of arenediazonium salts reactivity, the dediazonation, because a variety of complex mechanisms (heterolytic, homolytic and via aryne intermediates) operate leading to a wide range of products and slight modifications of the structures or of the reaction medium can change the pathway. The short Chapter 9, considered a philosophical interlude, is an attempt to insert the specific problem of diazochemistry into the general philosophy of the science concerning Logic, Psychology and a rather difficult word, Serendipity (the meaning can be discovered in the book). Chapter 10 is a survey of the applications in organic synthesis of the diverse heterolytic and homolytic dediazoniations,

including classical reactions, such as Sandmeyer, Meerwein and Gomberg-Bachmann, as well as the most recent developments (the references cover most of 1993). The host-guest complexes of arenediazonium salts with crown ethers and related compounds are discussed in Chapter 11, with particular cases of formation, structure, equilibria and properties of the complexes. Chapter 12 deals with one of the most important reactions of diazonium salts, the azocoupling (about 50% of all the industrial dyes manufactured during the last 120 years were produced by this reaction), this excellent chapter does not discuss the industrial aspects of the azo dyes, but rather highlights mechanistic understandings concerning diazo and coupling components, the acid-base pre-equilibria, kinetic isotope effects, mixing and diffusion effects and the influence of the reaction medium. The subject of the last Chapter, 13, is the replacement of protons in amines by arenediazonium ions with formation of triazenes.

This book represents the best available rationalization of aromatic diazochemistry; it is easy to read and indispensable to both academic and industrial chemists. It is particularly intended for researchers in the field of diazo chemistry, but it is also stimulating for organic chemists in general and should not be missing from any library.

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Activated Metals in Organic Synthesis. By P. Cintas. CRC Press: Boca Raton, 1993, 236 pp., hardback \$ 59.95 / £ 40.00. ISBN 0-8493-7863-X.

Metal-induced processes play a central role in synthesis but are sometimes difficult to carry out. Chemists often experience problems with the entrainment and the reproducibility of such reactions. Although this clearly emphasizes the importance of metal activation, a general and up-to-date treatise of this subject was missing. The present volume tries to fill the gap: rather than providing a comprehensive review, it compiles a plenty of examples which nicely illustrate that the use of an appropriately activated metal as the reagent may not only lead to significantly

improved preparative results but also to the discovery of new types of transformations.

The monograph is divided into two sections. The first one is an introduction to the "how" of metal activation. The different methods which have proven useful in synthesis are presented in detail, with the focus being on those techniques providing particularly performant metal samples. This includes the metal-vapor approach, Rieke's reduction method and modern variants thereof, the use of ultrasound, and the metal-graphite combinations. A few selected experimental procedures are incorporated into the text in order to familiarize the reader with the experimental set-up of the different techniques discussed.

Part two of the book then describes the preparative impact of such reagents. The material is divided into five chapters called "reductions", "reductive carbonyl coupling reactions", "addition reactions to carbonyl compounds", "cyclizations" and the "Bernet-Vasella reaction" (reductive ring-opening of deoxy halogeno sugars). This classification, however, is more or less formal: thus, one may regret that the discussion of the clas-

sical Grignard chemistry is spread throughout the book, while the Barbier one-pot version got its own chapter, although this modification has admittedly seen a renaissance in recent years. The author's selection among the wealth of different metal-induced transformations is selective rather than exhaustive. Modern advancements such as metal-promoted reactions in aqueous media, the McMurry alkene synthesis and the formation of enantiomerically pure building blocks from carbohydrates are covered.

This monograph on a rapidly expanding topic is written in a rather descriptive style with clear emphasis on the synthetic aspects of metal-promoted conversions, whereas the discussion of any mechanistic details as well as of the morphology of activated metals themselves is kept to a minimum. The quite extensive literature coverage up to 1992 makes it a useful source of information for the practicing organic chemist.

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