

## Book Reviews \*

**Handbook of Grignard Reagents.** Edited by Gary S. Silverman (Elf Atochem North America, Inc.) and Phillip E. Rakita (Elf Atochem Agri, SA). Marcel Dekker, Inc.: Monticello. 1996. xxiii + 708 pp. \$225.00. ISBN 0-8247-9545-8.

The book, entitled *Handbook of Grignard Reagents*, is 703 pages in length and is divided into 34 chapters. Each chapter describes an important aspect of Grignard chemistry, such as preparation, solid state structure, solution composition, mechanisms of reactions, reactions with organic substrates, transition metal catalyzed reactions, and polymerization reactions in which Grignard reagents are used as catalysts. In addition to these general areas, some more unique ones are covered, such as the use of Grignard reagents as bases,  $S_N2$  vs  $S_N2'$  reactions, di-Grignard Reagents, and asymmetric syntheses involving Grignard reagents. This treatment represents, by far, the most serious endeavor to update the classic contribution by Kharasch and Reinmuth, entitled *Grignard Reactions of Non-metallic Substances*, which was published in 1954. There have been some other attempts since 1954 to produce a treatise of the magnitude and competency of the Kharasch and Reinmuth book; however, these attempts have fallen woefully short until now. I believe that it has taken this long (forty-five years) because of the enormity of the individual contributions in the area of Grignard chemistry, the uncertainty of the mechanistic interpretation of even the simplest reactions, and the obvious inability of any one person to attempt such a feat. For this book, the authors have recruited over twenty-five colleagues to write specific chapters in order to reduce the task to the realm of possibility.

As a general statement, I believe it is fair to say that this book represents the first successful update of the Kharasch and Reinmuth book and, therefore, represents a major contribution, not just to organomagnesium chemistry, but also to the more general area of synthetic organic chemistry as well. It represents a monumental task, the completion of which should elicit a shout of gratitude from the entire chemical community.

A book of this type can read as a significant text with sufficient discussion in the development of each topic, or it can read like a series of chemical review articles which, although somewhat complete in references, lacks the discussion for a complete understanding of each topic. This book represents both. All the chapters are competent and well written, although some chapters are more authoritative than others. Some chapters were written by experts in the field while other chapters were written by authors who have not one cited contribution in the chapter that they wrote. It is interesting, however, that some of the chapters written by the less well-known authors are the better written contributions.

When there are many authors contributing to the same book, usually each chapter appears to be written entirely independently of the knowledge of the other contributions. This is not the case here, as the authors on many occasions refer to what is addressed in another chapter. Therefore, the continuity is quite good, and contradictions from chapter to chapter are not apparent.

There are some weaknesses to this book, however, that I should try to address. Most chapters are thorough, but not all are discriminating in the material presented. For example, covering old chemistry known to be incorrect at the expense of newer and more significant contributions can be a bit unnerving. In addition, there are some omissions of significant contributions; e.g., in Chapter 2 entitled Methods of Grignard Preparation, concerning the use of solvents, toluene + 2THF and 2NET<sub>3</sub> are not mentioned as solvent systems, yet these are the preferred commercial solvent systems for Grignard compounds, especially PhMgCl. This solvent system is safer than the systems reported, and the Grignard compounds are soluble at high concentration.

In the same chapter, there is no mention of RMgF compounds, only RMgCl, RMgBr, and RMgI. In no chapter was there sufficient discussion of the importance of the purity of magnesium metal with respect to its reactivity characteristics with organic compounds. There was no mention of the significance as to whether the Grignard reagent is made in excess magnesium or not and if the alkyl halide is used in excess and the importance of the size of the magnesium crystal used in the preparation reaction.

Two chapters in particular attempted a historical development of

their subject, e.g., Reaction Mechanisms of Grignard Reagents in which the history of the mechanism of reaction of Grignard reagents with ketones was described. After describing old chemistry in detail and the problems involved in determining the kinetics of the reaction, the history of the mechanism of the polar reaction stopped at 1968, and the subject of a radical mechanism involvement was developed further.

A most exciting time in this area revolved around the situation that although many reports (~300) had appeared concerning the mechanism of Grignard compound addition to ketones over a period of forty years and some reports involved kinetic studies, no one was able to resolve the complex kinetic data into a mathematical expression that allowed for the determination of the kinetic order of the Grignard reagent. Not knowing whether the reaction was first or second order, or even fractional order, in Grignard reagent, did not allow for an accurate depiction of a transition state necessary for a mechanistic understanding of the reaction.

An important paper appeared in 1971 that settled this problem when it reported, for the first time, kinetic data that were interpretable, showing the reaction to the first order in Grignard reagent and providing a detailed mechanism which, 26 years later, has not been questioned. The same article further showed why previous kinetic data could not be interpreted, namely, (1) the composition of Grignard reagents was unknown, (2) the Grignard reagent concentration had to be very low so that only monomeric species were present, (3) the Grignard reagent had to be made with an excess of alkyl halide so that MgH<sub>2</sub> was not present in the Grignard reagent, and (4) the derivation of the differential rate expressions had to take into account that the product of the reaction before hydrolysis (ROMgX) was strongly complexed to the RMgX reactant (to form an ROMgX·RMgX alkoxy-bridged dimer) which accounts for the disappearance of RMgX not only in its reaction with the ketone, but also in its reaction with the product. Unfortunately this contribution which represented the first clear understanding of the polar mechanism involving a Grignard reagent and a ketone was not presented in its historically appropriate place but rather was presented in this chapter as the very last reference after all other aspects of the radical nature of the reaction had been discussed. Hence, the excitement that existed in this area over a period of forty years and the resolution of an important mechanistic problem in organic chemistry were lost in the historical development.

In addition, the first demonstration by <sup>1</sup>H NMR of distinct RMgX and R<sub>2</sub>Mg species in Et<sub>2</sub>O and THF was referenced, but its importance not described, although up until that point Grignard reagents were thought not to contain RMgX species. The classic isotopic labeling studies of Dessy that reportedly proved that RMgX species did not exist in solution, studies that completely detoured the mechanistic interpretation of Grignard reactions for a decade, were refuted by the <sup>1</sup>H NMR studies. The Dessy isotopic labeling experiments were not mentioned, in spite of their enormous effect in the thinking about Grignard reagent composition and mechanisms of reactions.

The discussion of the composition of Grignard reagents in Et<sub>2</sub>O and THF was inadequate considering the vast amount of information available on the subject. The reader was not exposed to the fact that monomer-dimer-trimer species exist at various concentrations depending on the nature of R, X, and the solvent. This is a very important piece of information. No mention is made of the fact that the intermediate ketyl species involved in the reaction of a Grignard reagent with a ketone has been identified by ESR by comparison of spectra of the reaction in progress with those of the particular species made separately. In the discussion of the mechanism of the formation of a Grignard reagent, no mention is made of the report that it has been established by radical trapping experiments using DCPH that one can show that (in the case studied) approximately 25% of the radicals do leave the surface and return. This report is significant in that controversy continues to this day as to whether or not radical species leave the surface of the magnesium during the preparation of Grignard reagents. In the chapter on metal-catalyzed reactions, Scheme five on page 621 involves the unusual stereoselectivity in the alkylation of 4-*tert*-butylcyclohexanone with organometallic reagents; the reasons for such stereoselectivity was first described in detail by another author years before the present reference.

In spite of some shortcomings, nevertheless this book represents a

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major contribution in organic chemistry and will certainly be appreciated by every practicing synthetic organic chemist.

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**Comprehensive Heterocyclic Chemistry II: A Review of the Literature 1982–1995. 12 Volume Set.** Editors-in-chief: Alan R. Katritzky, Charles W. Rees, and Eric, F. V. Scriven. Elsevier (Pergamon): Oxford, 1997. 11 856 pp. \$6345.00. ISBN 0-08-042072-9.

With this large set Pergamon Press continues its efforts to present broad, scholarly overviews of major areas of chemical research. *Comprehensive Heterocyclic Chemistry II* (CHEC-II) is a "sequel" to 1984s *Comprehensive Heterocyclic Chemistry*, which attempted to summarize the current state of research and the associated literature through 1982. Together these two sets offer chemists an alternative means of accessing the formidable literature dealing with heterocyclic substances. Defined as cyclic organic compounds that possess one or more non-carbon ring atoms, heterocycles are an enormously important and almost limitless class of compounds, prominent in most areas of biological, pharmaceutical, natural products, and industrial chemistry. Of over 15 million compounds registered by Chemical Abstracts Service, over half are heterocyclic.

CHEC-II is designed to complement, rather than replace, the original 1984 set. The general chapters are not repeated, but the scope has been expanded to include areas omitted from the earlier work. The arrangement of chapters has been slightly revamped with the intention of making the set more logical and easier to use. 263 chapters cover the structure, reactions, synthesis, and uses of various types of heterocycles. The volumes are ordered to follow increasing ring size.

An interesting feature of CHEC-II is its unique method of providing literature references. As any reader of the chemical literature knows, traditional superscripted footnotes require a great deal of page-flipping from the text to the reference list, an inconvenience that is amplified in review-type publications that contain many such citations. The editors have followed the pattern first devised for the 1984 work, wherein the literature reference is encoded in brackets within the text itself, using a format of (YEAR/PUBLICATION CODE/PAGE). For example, the reference (87TL2827) translates as *Tetrahedron Letters*, 1987, page 2827. Once the reader learns the principal publication codes, which are printed inside the covers of all volumes, it becomes easy to proceed directly to much of the original literature without turning to the master reference list. In a work that contains over 50 000 total references, this is a useful time-saving device. (Each volume also contains a full reference list in traditional ACS format, arranged chronologically.)

Volumes 10 and 11 comprise the indexes. The Author Index compiles over 75 000 names from the references, and refers the reader to the volume and page number in the text where an author's publication was cited. The index entry also includes the individual publication's reference code. Also in Volume 10 is the Ring Index, where compounds mentioned in the text are classified by their fully unsaturated parent compound, and arranged by *Chemical Abstracts'* Ring System convention. Particularly useful is the Ring Index's distinction between primary and secondary entries: a boldface entry denotes text that discusses a system extensively as opposed to mentioning the system in context of another topic. Volume 11 is the Subject Index, with 80 000 keyword terms, compound names and classes, and other general topic headings. It is evident that much thought went into the indexes and reference system, and the usefulness of the work depends on them.

With competition from well-established reference works such as *Beilstein* (the current Fifth Supplement of which is devoted exclusively to heterocycles described between 1960 and 1979), *Methoden der Organischen Chemie* (which emphasizes synthesis), and large monographic series like Wiley's *Chemistry of Heterocyclic Compounds*, CHEC-II must offer a different approach to organizing the current state of knowledge. By and large, it succeeds. It does not attempt to describe every single heterocycle ever discovered or synthesized, nor does it provide a reference to every journal article or patent ever published on them, but rather tries to point to the most important and representative of them. Its logical organization and text-based approach make it easier for nonspecialists and advanced students to consult, and its indexes

are thorough and very helpful. Chemists will probably find it a handy entry point into the vast literature on the topic.

As with other Pergamon sets in this series, the high price will discourage purchasers outside of relatively well-funded academic and corporate libraries. (Librarians should note that the price works out to \$0.53 per page, comparable to the discipline's more expensive journals.) Though mainly intended for use alongside the now out-of-print 1984 edition, CHEC-II is a self-contained work. The publisher claims that CD-ROM versions of both sets will be available later in 1997.

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**Henderson's Dictionary of Biological Terms, 11th Edition.** Edited by Eleanor Lawrence. Wiley: New York, 1995. ix + 693 pp. \$39.95. ISBN 0-470-23507-1.

This is the eleventh edition of this dictionary and now contains 23 000 headwords that encompass a wide array of biological sciences including zoology, botany, ecology, biochemistry, the environment, and medicine. Completely revised, this dictionary provides headwords covering all biological specialties; figures that help clarify complicated terms; a classification of plants, animals, and more; a Latin and Greek derivations appendix; structural formulae; a reference of units and SI prefixes; and acronyms.

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**X-Ray Analysis and Structure of Organic Molecules, 2nd Corrected Edition.** By Jack D. Dunitz (ETH-Zurich). VCH: New York, 1995. 514 pp. \$70.00. ISBN 3-906390-14-4.

This volume is written in two parts: Part I is a complete guide to current methods of determining the crystal structures of small or medium-size molecules, the treatment of results, and the experimental aspects of X-ray analysis. Part II explores crystal structure analysis and chemistry, electron density distributions in molecules, geometric constraints in cyclic molecules, and conformational maps and space groups. Previously published by Cornell University Press, this is a newly updated and corrected second edition published by VCH.

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**Silicon-Containing Polymers.** Edited by Richard G. Jones (University of Kent at Canterbury). The Royal Society of Chemistry: Cambridge, 1995. xiii + 197 pp. \$88.00. ISBN 0-85404-745-X.

This book is the result of the Silicon-containing Polymers International Symposium at the University of Kent held July 6–8, 1994. The contents reflect the growing interest in polymers since they are used as molding materials, rubbers, ceramic precursors, in lithography and reprography as photosensitive materials, as conducting polymers, and other applications. The book covers the synthesis, modification, characterization, properties, and applications of polysiloxanes, polysilylenes, polysilazenes, and organosilicate derivatives.

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