

Book Reviews

Ketenes. By T. T. Tidwell. Wiley: New York, 1995, 665 pp., hardback. £ 70. ISBN 0-471-57580-1.

The aim of the present book is to offer a comprehensive up-to date report on ketene chemistry in general based upon more than 2500 original papers (!). A brief introduction is followed by five main chapters covering structure, bonding and thermochemistry (chapter 1), spectroscopy and physical properties (chapter 2), preparation (chapter 3), types of ketenes (chapter 4) and reactions (chapter 5). All chapters are divided into several sub- and sub-subchapters, respectively. To avoid any confusion it is important to note that the appropriate references are generally listed at the end of any subchapter or even sub-subchapter.

The book starts with a concise but informative historical retrospect mentioning all previous reviews on the topic since the famous monograph of *Staudinger* from 1912. In chapter 1, theoretical studies of ketenes, as well as geometries and molecular structures, are discussed extensively. The number of original papers coming from the authors desk reveal his high competence in that particular area. A brief but very useful overview on ^1H -, ^{13}C - and ^{17}O -NMR spectroscopic data as well as UV, PE and MS measurements are reported in chapter 2. In addition, IR data, which play an important role in identification and characterization of ketenes, in particular with highly unstable derivatives isolable at very low temperatures only (matrix isolation), are listed exhaustively exhibiting the specific carbonyl stretching frequencies together with corresponding original reference numbers. Chapter 3 offers an abundant overview on methods of ketene preparation e.g. from ketene dimers, from carboxylic acid derivatives (halides, esters), thermal and photochemical cleavage of cycloalkanones and -alkenones, from dioxinones and heterocyclic 2,3-diones. Particular emphasis is given to generating ketenes via thermally and photochemically initiated *Wolff* rearrangement of diazoketones (112 references). Furthermore, some more exotic approaches to ketenes e.g. from alkenylcarbene metal complexes are also reported. In all those sub- and sub-subchapters a lot of details are presented based upon more than 450 original papers. Chapter 4 is the most voluminous one, it requires nearly half of the whole book since within approx. 300 pages all known types of ketenes are described. It is extremely useful that all ketenes named in several

subchapters are listed in tables where one can find for any particular compound its structural formula, most efficient methods of preparation and the corresponding original reference. Alkyl-, alkenyl- and alkynylketenes as well as aryl- and cyclopropylketenes are presented, followed by acyl- and imidoalkylketenes. Ketenes with charged, radical or carbenic side chains as intermediates and fulvenones are discussed in detail. N, O or halogen substituents in general destabilize ketenes while silyl-, germyl- and stannylketenes as well as phosphorous- and arsenic-substituted ketenes are remarkably stable. This also stands for sulfurketenes. After a brief subchapter describing metal-substituted ketenes, bisketenes and, finally, cumulenones (e.g. carbon suboxide) are presented in a concise way. Chapter 5 deals with reactions of ketenes. After brief statements on oxidation/reduction, photochemistry and thermolysis, the main subchapter (110 pages) describes all kinds of cycloaddition reactions observed with ketenes in greater detail. Special emphasis is directed to an extensive discussion of preparative and mechanistic aspects of [2+2] cycloaddition reactions, in particular the classical problem synchronous versus two-step process is illustrated in an up-to-date manner (229 references !). Finally, mechanistic and preparative aspects of nucleophilic as well as electrophilic additions to ketenes are discussed in some detail, followed by radical reactions, polymerization and a brief but instructive discussion on stereoselectivity in ketene reactions.

A great number of figures, tables, equations and formula schemes help the reader to get a rapid and comprehensive entrance to any specific topic of ketene chemistry. Within all chapters relevant literature data are presented exhaustively which is extremely helpful for readers wanting to go into further details. Summarizing, this monograph provides an excellent overview on all aspects of ketene chemistry and is very useful for synthetic chemists from academic as well as industrial provenance. It is also recommended for graduate and post-graduate students engaged in research work in that area.

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Lithium Chemistry. A Theoretical and Experimental Overview. Edited by A.-M. Sapse, P.V.R. Schleyer. Wiley: New York, 1995, 595 pp., hardback. £ 71. ISBN 0-471-54930-4.

The bad news first. This book does not deal with synthesis nor does it describe methods useful for the preparation of new compounds. It focuses on the structures of organic and inorganic lithium derivatives as determined by mathematical, spectroscopic or physicochemical investigations. Nevertheless, the book may also prove valuable in the hands of the laboratory practitioner, since it provides a wealth of inspiring information on lithium compounds in general and organolithium reagents in particular.

The eleven chapters of the book address these topics: Structures of simple organolithium compounds (Streitwieser, Schleyer *et al.*, 44 pages), Aggregation (Sapse *et al.*, 21 pages), Hydrogen and lithium bridges (Scheiner, 21 pages), Matrix isolated lithium atoms (Manceron *et al.*, 35 pages), Heteronuclear Overhauser effects (Bauer, 46 pages), Thermochemistry (Liebmann *et al.*, 21 pages), Carbenoids (Boche *et al.*, 32 pages), Structures of lithium (pseudo)halides (Snaith *et al.*, 67 pages), Structures of lithium alcoholates, enolates, amides, silanides and higher isologues thereof such as lithium thiolates, phosphides and stannides (Power *et al.*, 98 pages), Crown ether and cryptand complexed lithium salts (Bartsch *et al.*, 84 pages) and polyolithium compounds (Maercker, 101 pages). The last contribution is certainly the one having the strongest link to the laboratory although the German spoken reader may prefer the article which has been published by the same author in the Houben-Weyl Handbook Vol. *E19d* (118 pages), since it appears to be more up-to-date and contains also many working procedures. The chapter on thermochemical issues is without doubt one of the highlights - what a pity that all energy data are given in consumer unfriendly kJ/mol units (whereas all other authors use kcal/mol). The three introductory chapters illustrate the potential of the computational approach, but would be even more instructive if pertinent experimental (mainly spectroscopic) results had been covered less sporadically.

In view of the price, it would be naive to assume many private copies to be purchased. Therefore, it is to be hoped that the book finds a place in any major chemistry library.

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Encyclopedia of Reagents for Organic Synthesis. Edited by L. A. Paquette, S. D. Burke, R. M. Coates, R. L. Danheiser, S. E. Denmark, D. J. Hart, L. S. Liebeskind, D. C. Liotta, A. J. Pearson, H. J. Reich, J. H. Rigby, W. R. Roush. Wiley: Chichester, 1995, 6223 pp., hardback. £1750. ISBN 0-471-936235.

The Encyclopedia of Reagents for Organic Synthesis, consisting of eight volumes and covering more than 3000 of the most important reagents in organic synthesis, has been accomplished through the work of an international board of editors and advisors, and over 1000 authors, all experts in their field. This high calibre of contributors is reflected in the high quality of this publication.

The purpose of the volumes is "to present an authoritative and systematic description of the utility of all reagents used in organic chemistry", and its goal, to create a reference work where the "retrievability of useful information concerning any specific reagent is made facile". Both of these criteria have been achieved through a highly detailed survey of reagents which are listed alphabetically according to IUPAC nomenclature, and a comprehensive index of more than 600 pages. The volumes are well produced and clearly presented with high quality structures and clear, concise text. Extensive referencing covers literature up to and including citations from 1994. The text is clearly written, comprehensive, extensively literature-referenced and includes frequent illustrative schemes. Each reagent listed is described in an independent article which is usually devoted specifically to a single reagent, although very closely related reagents may be dealt with in the same article, e.g., phthalimide and potassium phthalimide. Cross-referencing to other reagents having their own entries within the encyclopedia is by means of bold italics, providing a quick and easy route to additional information.

Each entry comprises a masthead containing a structural representation of the reagent, thus, the beginning of each new entry is instantly obvious. When it exists, a review article is cited in the title as the first literature reference. Useful data, such as the molecular formula and weight, is followed in parentheses by a brief summary of the reagent's uses (again with literature references). Information on physical data, solubility, handling, storage and precautions, and the form in which the reagent is supplied in is given; methods of analysis of reagent purity, purification, and preparation also appear where relevant, and all are adequately referenced to fundamental reviews and papers. Alternative commonly used names for the reagent are also included. Thus, the experimental chemist is provided with immediate knowledge and with minimum effort.

The masthead is followed by a more in-depth discussion of the uses characteristic of each reagent, including specific examples involving the reagent in question. Uses are classified under titles such as reaction type (named and unnamed reactions), transformations which can be performed, reaction with specific substrates and formation of particular products. Again extensive coverage of the relevant literature is present. A brief introduction is sometimes included, giving a useful insight into the reagent; a more general discussion may be employed to discuss the reagent in a more overall way. Useful advice may also be added, e.g., order of addition of reagents, all of which is directed towards aiding the work of the practical chemist. Major uses of the reagent are followed by related reagents, where applicable, which can also be referred to within the encyclopedia.

To achieve the aforementioned goal of facile retrievability of information, an exhaustive index is necessary. This has been achieved by four separate indexes which appear in Volume 8. The reagent formula index provides easy access through molecular formulas arranged alphabetically and in the order of increasing number of carbon atoms. This is invaluable when searching for a reagent without having to know the IUPAC name. The reagent structural class first provides a shorter, more general list of reagents, e.g., barium reagents, bases, quinones, which refers to an ensuing, more detailed list of reagents having this specific structure. The reagent function index provides a means of finding entries according to their action, e.g., alkylating agents, desilylating reagents, ring expansion agents, and the subject index lists entries by reaction type, named reactions, general substrates or products, specific substrates or products. Particularly useful is the appearance of reagents under some of their more commonly used abbreviations. The IUPAC-named reagents appear in bold typeface.

To summarize, the Encyclopedia of Reagents for Organic Synthesis is a reference text providing easy access to an excellent, very thorough survey of reagents for organic synthesis. Although reasonably priced if one considers the amount of time, effort and energy which must have gone into the preparation of this work, it is likely to be out of the price-range of smaller parties. It is, however, an essential purchase for, and will make an invaluable and indispensable addition to, any library used by experimental organic chemists and, indeed, chemists from all disciplines, where it will provide a sound accompaniment to existing primary literature; its use is to be strongly recommended to anyone undertaking organic synthesis.

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Free Radicals in Organic Chemistry. By J. Fossey, D. Lefort, J. Sorba. Wiley: New York, 1995, 307 pp., paperback. £ 18.99. ISBN 0-471-95496-9.

The first organic free radicals were described at the beginning of this century and their importance was soon recognized in industrial chemistry. With the advent of electron paramagnetic resonance (EPR) spectroscopy, the technique capable of detecting even very short lived radicals, the role of organic free radicals in biochemical research has also become more and more recognized. On the contrary, free radical chemistry is usually underrepresented in higher education and it is yet to receive the attention it deserves in chemistry graduate courses. This is also true for most organic chemistry textbooks in which the discussion of organic free radicals is usually limited to polymerization processes of industrially importance.

Therefore, the comprehensive discussion of free radical chemistry presented by J. Fossey, D. Lefort, and J. Sorba is essential not only for chemistry students, but for a wide range of present and future professionals in a wide field ranging from clinical biochemists to industrial technologists: for anyone who needs to have a guidance in understanding organic free radical chemistry.

The remarkable achievement of the authors is that they were able to fulfill the need for both teaching the principal phenomena and applications of free radical chemistry.

The book consists of 26 chapters which are arranged into four parts. Part I is a brief but complete treatise of general concepts and basic principles providing a firm basis of further applications. It also deals with detection of free radicals by spectroscopic methods. Principles of EPR spectroscopy and derivation of various spectral hyperfine structures as well as that of the usually less discussed Chemically Induced Dynamic Nuclear Polarization (CIDNP) are clearly explained. A special forte of this part is the discussion of the relationship between the geometric and electronic features of the radical and its reactivity and stability. Part I is concluded by a chapter on the importance of halogen, heteroatom, metal and other non-carbon radicals in organic synthesis. In Part II several types of radical reactions, such as substitutions, cyclizations, rearrangements and fragmentations are classified and explained. The role of free radicals in biochemistry is treated only in a short but well written chapter. Being recently in the focus of interest of biochemistry, specially of clinical stress studies, this topic is treated too briefly. Similarly, important reactions of nitrogen monoxide radical, the molecule of 1992 may have deserved a few

lines. with organic compounds in biology. Part III is an excellent collection of applications in synthesis. The section gives a well chosen overview for the radical transformations of functional groups and chemical bonds in synthetic organic chemistry. This part certainly provides many new ideas for reader who planning to solve new organic synthetic problems by radical methodology. Part IV is a comprehensive collection of references. It contains selections of relevant references from free radical chemistry to direct readers who also wish to consult the original publications. The book also contains 29 useful tables of physical data and constants, such as

rate constants, ionization potentials, bond energies. Overall, this didactic, well written book guides the readers into the rapidly expanding field of free radicals with clear style and unquestionable expertise. It is not only valuable for personal use in graduate studies of free radical chemistry but it should not be missing from chemical and science libraries either.

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