

formation.¹⁶ This is consistent with the fact that the cyclopropyl group is acid weakening in benzoic acids, where resonance is possible, but acid strengthening in acetic acids where resonance is unimportant.¹⁷

Thus cyclopropyl gives a widely varying effect on electrophilic additions to olefins. The variation of this effect helps to define the transition state structure for different additions and promises to prove useful as a guide to the evaluation of the mode of attack of different electrophiles on olefins.¹⁸

(16) (a) Y. E. Rhodes and V. G. DiFate, *J. Amer. Chem. Soc.*, **94**, 7582 (1972); (b) B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (c) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(17) (a) R. C. Hahn, T. F. Corbin, and H. Schechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968); (b) Y. E. Rhodes and L. Vargas, *J. Org. Chem.*, **38**, 4077 (1973).

(18) After submission of this manuscript a study appeared of the hydrochlorination and oxymercuration of 2-cyclopropyl-3-phenyl-2-

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butene (G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Amer. Chem. Soc.*, **96**, 3548 (1974)), in which the only observed products appeared to result from preferential generation of the cationic center next to the cyclopropyl group. Also we have learned (A. J. Kresge and C. I. Young, unpublished results privately communicated) that in hydrolysis of vinyl ethers, RC(OMe)=CH_2 , the rates of hydration are essentially the same when R is cyclopropyl or methyl, and about six times less when R is phenyl. Similarly cyclopropyl has been found to be less effective at assisting the formation of the bridged 2-adamantyl cation than is ethyl (D. Lenoir, *Chem. Ber.*, **106**, 2366 (1973)). All of these results are in complete accord with the interpretations proposed herein.

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Book Reviews

Gas-Chromatographic Analysis of Trace Impurities. By V. G. BEREZKIN and V. S. TATARINSKII (A. V. Topchiev Institute for Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow). Translated from Russian by J. E. S. BRADLEY (University of London, London, England). Consultants Bureau, A Division of Plenum Publishing Corp., New York, N. Y. 1973. ix + 177 pp. \$29.50.

This book discusses the major aspects of gas chromatographic determinations of trace impurities. Methods are discussed in terms of general principles, and specific methods are given only when needed to illustrate the methodology. There is no attempt to give a comprehensive listing of methods for specific materials. The book is intended for those who are unfamiliar with the field of gas chromatographic trace analysis. The authors' treatment of subject matter does, however, assume that the reader has some familiarity with the basic concepts and practices of gas chromatography.

The book opens with a general discussion of the problems associated with gas chromatographic separation of impurities. This is followed by a chapter on the use of large samples to achieve high sensitivity with emphasis on the relationship between sample size and column performance. The next chapter presents a general discussion of gas chromatography detectors with emphasis on ionization and thermal conductivity detectors. A subsequent chapter is devoted to the use of selective sorbents and selective detectors, such as electron capture and flame-photometric detectors. The next topic presented is the use of column temperature programming to enhance trace component separations. This is followed by a chapter on reactive analytical gas chromatography. The next topic discussed is that of sample accumulation or concentration methods. This chapter is subdivided into (1) chromatographic methods of impurity enrichment and (2) other techniques. The latter includes a variety of enrichment methods which are based on adsorption or condensation of trace impurities and can be used in conjunction with analysis by gas chromatography. The factors that must be considered in quantizing gas chromatographic analyses are discussed in the next chapter. The final chapter is devoted to a discussion of basic methods of preparing standard mixtures for calibrating chromatographic systems. Although each chapter is well documented with references, use of the book is hampered by the lack of a subject index.

The book makes one aware of the major problems encountered in performing trace analysis and should be especially helpful to one who is beginning work in this area. The chapters on reaction gas chromatography, accumulation methods, and methods of preparing calibration mixtures are particularly well done. The book provides a good access to the older (pre-1970) literature on gas chromatographic trace analysis and gives key references (through 1969) where detailed procedures for major methods of analysis can be found.

For one who is experienced in gas chromatographic trace analysis and is familiar with the literature, it is doubtful that the book would be of much practical value.

The main shortcoming of the book is that it does not represent the current state-of-the-art of gas chromatographic methods for trace analyses. Since publication of the original Russian text in 1970, significant technological advances have been made—particularly in the area of environmental analyses. Unfortunately, the current English translation does not include an updating of the literature. For example, the important role of capillary gas chromatographic methods in trace analysis is not discussed. Also missing are discussions of the recent major advances in the use of microcoulometric and flame-photometric detectors and combined gas chromatographic-mass spectrometer techniques. In column technology, there have been significant developments in methodology based on the use of newer types of column packings, such as porous polymers and supports with chemically bonded liquid phases. In the area of instrumentation, specialized gas chromatographic instrumentation is now available which enables trace analysis of many materials to be made rapidly, accurately, and automatically. These newer methods have supplemented or replaced many of the older gas chromatographic methods discussed in the book. Therefore, for optimum benefit from the book, the reader should supplement it with a current search of the literature.

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Free Radicals. Volume 2. Edited by J. K. KOCHI (Indiana University). Wiley-Interscience, New York, N. Y. 1973. xx + 906 pp. \$42.50.

The second and last volume of the monograph includes the remaining three parts (in the review of Vol. 1, *J. Amer. Chem. Soc.*, **95**, 8493 (1973), *four volumes* should be replaced by *four parts*).

Part 2, Free Radical Chain Reactions, consists of chapters on homogeneous liquid-phase autoxidations (J. A. Howard), addition to multiple bonds (P. I. Abell), atom-transfer and substitution reactions, halogenation (M. L. Poutsma), and aromatic substitution (M. J. Perkins).

Part 3, "Structure and Energetics," consists of chapters on thermochemistry of free radicals (H. E. O'Neal and S. W. Benson), the structure and stereochemistry of free radicals (L. Kaplan), structure of free radicals by ESR spectroscopy (H. Fischer), and solvation and association (J. C. Martin).

Part 4, "Free Radicals with Heteroatoms," consists of chapters on nitrogen-centered radicals (S. F. Nelsen), phosphorus radicals (W. G. Bentrude), oxygen radicals (J. K. Kochi), sulfur-centered radicals (J. L. Kice), group IVB radicals (H. Sakurai), and bridged free radicals (P. S. Skell and K. J. Shea).

A subject index is appended. An author index would have been useful.

The standard of the reviews is quite high, and the literature is reviewed in most chapters up to and including 1972. However, Kaplan's monograph "Bridged Free Radicals," 1972, is not quoted in the chapter on this topic, but in other chapters. Chapters of Part 4 had to avoid including material available in other recent monographs and at the same time to update them while remaining self-consistent. This was achieved in most of them.

This second volume is more comprehensive than the first one, and deserves the same favorable recommendation.

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Workbook in Organic Chemistry. By T. A. GEISSMAN (University of California, Los Angeles). W. H. Freeman and Co., San Francisco, Calif. 1972. xii + 245 pp. \$4.95 (paperbound).

The author's purpose in writing this workbook is to give the organic chemistry student a supplementary text to review and reinforce his understanding of organic chemistry, and to learn how to approach the solution of various types of problems relating to structure, mechanisms, and syntheses.

The text is well written and should serve as a good supplement to a basic or intermediate organic chemistry text. The author's choice of topics in some areas is perhaps better suited to an intermediate organic chemistry course rather than a basic organic course, such as is given in my college. For example, most basic organic courses never mention topics such as the Stobbe Condensation, Mannich Reaction (Part 4), or C-Alkylation with Enamines which the author discussed in Part 6. Based on my own personal experience in teaching both basic and advanced organic chemistry courses at the college level, I feel that this workbook is better suited in areas such as mentioned above for an intermediate rather than basic organic chemistry course.

Overall, the author has selected a good choice of exercises and varied problems. The book contains answers and solutions to all the exercises, as well as some sample illustrative problems. Each section has a brief textual discussion reviewing the essential concepts of the material.

Part 10 on the Balancing of Organic Oxidation-Reduction Equations is well-written and is particularly well suited to a text of this type, as students always seem to have trouble with this topic. Part 11 on Planning the Synthesis of an Organic Compound and Parts 12 and 13 dealing with Problems including Spectral Data, Roadmaps, and Structure Proofs are excellent in that they teach the student how to interpret and use experimental data in problem solving. Some of the exercises presented in Part 13 are difficult and should be left for the superior students.

I noted that the answer to exercise 3.2 depicts cyclohexane as a flat hexagon; it would be better to draw the chair conformation for cyclohexane and emphasize the axial and equatorial substituents in cis and trans isomers as is done in Exercise 3.3. I agree with the author in that some topics must be omitted in such a workbook. However, I do definitely feel it essential to include discussion of the *R* and *S*, and *E* and *Z* configurations in Part 3 on Stereochemistry. Thallation, which is a relatively new and significant synthetic tool, should be included in Part 9 on Aromatic Substitution Reactions. The student should be made aware of the similarity of the Wittig reaction to the aldol condensation, since both reactions involve carbanion species.

In summary, I am of the opinion that the text is well written as a review book. It is on par with other workbooks I have used. As my comments have indicated, the essential concepts and principles are accurately presented, except for the few suggestions cited above. If the potential user can realize that the selection of topics has been limited and that some topics presented are beyond the basic organic course level, this text can serve as a useful supplementary workbook to the one-year basic organic chemistry course.

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Radiation Chemistry of Monomers, Polymers, and Plastics. By JOSEPH E. WILSON (Bishop College, Dallas, Tex.). Marcel Dekker, Inc., New York, N. Y. 1974. xi + 633 pp. \$49.50.

Radiation chemistry—a field of research effort now comprising over 15,000 literature references—has shown itself to be of both fundamental and practical interest. An intensely active portion of the work is in the field of polymer radiation chemistry. "Radiation Chemistry of Monomers, Polymers, and Plastics" addresses itself directly to this portion of the field. It is radiation chemistry as seen by those involved with, or hoping to be involved with polymer chemistry. True to its title, the book does not concern itself with

biochemical applications of radiation or with more than a mention of the effects of radiation on inorganic systems. The flavor is one of being both a textbook and a review. Some chapters deal only with principles of radiation chemistry, while other portions of the book are much more characteristic of a reference work.

Early chapters acquaint the reader with types and sources of radiation, the interactions of radiation with matter, and the immediate chemical effects of these interactions. In regard to these subjects, it is very helpful to have a number of problems, some of which are solved, as examples of the quantitative aspects of the subject. Within these early chapters is also a summary of fundamental and theoretical radiation chemistry. For a thorough understanding of these matters the reader will probably want to turn elsewhere within the radiation chemical literature. What this section provides, however, is a glimpse at the fundamentals to provide a better understanding of the ultimate effects of radiation in the polymeric systems.

Polymerization under the influence of high-energy radiation is the subject of the next several chapters. Here we find both the characteristics of a text and those of a review. The descriptive material includes polymerization in homogeneous systems, the solid state, emulsions, and thermosetting systems. It is very helpful to find the relationship between concepts of free radical chemistry and the somewhat more specialized situations to be found in radiation chemistry. Similarly, the discussion of kinetics during polymerization by radiation is a great aid in understanding the application of radiation to the better known polymer chemistry field.

The remainder of the book provides detailed reviews on the subjects of irradiation of polymers, including cross-linking and degradation, and radiation grafting of monomers on polymer films or on polymer fibers.

Where the data available in the literature appear to require more than the intended chapter size, extensive tables with bibliographies are employed. In those chapters where this method has been used, the book is usable as a reference tool in updating the previous works on this subject.

Of those subjects covered by this book the one which seems the weakest is the technology of irradiation itself. The data supplied, while accurate, are rather badly out-of-date. Within the past years great strides have been made in the fabrication of reliable electron-accelerator machines and low-cost radioisotope γ sources. The descriptions of available items and the cost of them are much better found in the more recent chemical engineering literature.

In summary, the reader will find in this book an adequate and often excellent background in the application of radiation to polymer chemistry, together with an introduction into other allied aspects of radiation applications.

David E. Harmer, *The Dow Chemical Company*

Inorganic Chemistry of the Transition Elements. Volume II. B. F. G. JOHNSON (Cambridge University), Senior Reporter. The Chemical Society, London. 1973. xvi + 501 pp. £9.50.

This volume is another of the Specialist Periodical Reports by the Chemical Society, comprehensively covering the chemistry of the transition elements including the lanthanides and actinides from October 1971 to September 1972. The material is limited to preparative and characterization procedures with a minimal amount of critical discussion. The chapter titles and reporters are: (1) The Early Transition Metals (C. D. Garner); (2) Elements of the First Transitional Period (R. Davis); (3) The Noble Metals (L. A. P. Kane-Maguire); (4) The Lanthanides including Scandium, Yttrium, and the Actinides (J. A. McCleverty).

There is no subject index, but the book has an extensive table of contents which displays the organization of the material by metals. Then each oxidation state of the metal is covered with respect to the ligands involved. About 4800 authors are cited, a fact that indicates the extensiveness of the work in this field. This volume is a good direct and convenient source of reference and has an actually amazing breadth of material. It is entitled Inorganic but also covers a good deal of Organic chemistry of the metals. However, in spite of the broad coverage, two rather significant recent developments were not covered, namely, work on transition metal atom (vapor) chemistry, and uranocene and related materials. Publications in these areas might be considered more "organically" oriented but certainly would fit nicely into this volume.

By its nature the book is not easy to "read through," but it must be highly recommended as a reference text for almost all transition metal and rare earth chemists.

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