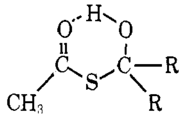
are completely opposite to the previously described experiment, and inconsistent with the triplet addition–hydrogen migration mechanism there suggested. A consistent mechanism is triplet abstraction followed by radical pair recombination, dominated by a strong, matrix-imposed "memory" effect which favors collapse at the initial site of abstraction. A direct (singlet) insertion origin of this olefin is less likely because the nonobservance of this product at −40 °C (where cyclopropanation is the major reaction pathway) would require that singlet insertion have a lower activation energy than (presumably singlet) addition.

We do not know what contaminant gave rise to the strong ^{13}C absorption at δ 37.8 [C(3)] in the original experiment; attempts to reproduce this result have failed. Preliminary repetitions of the phenyldiazomethane-^{13}C-labeled isobutene experiment give conflicting results. Pending a detailed reinvestigation, the triplet addition–hydrogen migration mechanism must be considered questionable in this case too.

It should be noted that the reported product distributions are unaffected by the present revision; alkene formation due to triplet phenyl and phenylmethylcarbenes, at the expense of cyclopropanation, is indeed the dominant reaction of these carbenes in isobutene matrices.

Dynamic Nuclear Magnetic Resonance Spectroscopy. Carbon–Sulfur p–p π-Bonding and Conformational Equilibria in Thioacetic Acid [*J. Am. Chem. Soc.*, **99,** 2803 (1977)]. By ERIC A. NOE, Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

The acetyl methyl signals observed at −50 °C for thioacetic acid (**1**) in acetone-d_6 solution are due to the addition product **4a** and unreacted **1**, rather than *E* and *Z* isomers of **1**, as previously assigned. The low-temperature (−90 °C) ^{13}C spectrum of thioacetic acid (720 mg) in acetone (2.4 g) shows peaks assigned to **4b** at δ 199.7, 86.1, 31.4, and 30.4, relative to tetramethylsilane. Other good evidence for the formation of **4** has been reported by T. Horii, S. Kawamura, and J. Tsurugi [*Bull. Chem. Soc. Jpn.*, **45,** 2200 (1972)]. I thank Dr. Horii for bringing this work to my attention.



4a, R = CD_3
b, R = CH_3

The coalescence temperature for a solution of thioacetic acid in $CHClF_2$ (ca. 0.2 M at −78 °C) was −136 °C, corresponding to rotational barriers of 7.0 and 7.3 kcal/mol. Evidence for a first-order process (rotation about the C–S bond, rather than intermolecular exchange of the SH proton) was obtained from the following two experiments: (1) The coalescence temperature did not change, within experimental error, when the concentration was increased or decreased by a factor of 2. (2) Coalescence for exchange of the SH protons in an equimolar mixture of thioacetic and thiopropionic acid (**5**) in $CHClF_2$ (approximately 0.2 M in each compound) occurs at −80 °C ($\Delta\nu_{SH}$ = 5.2 Hz). This result shows that, under these conditions, intermolecular exchange of the acidic proton between **1** and **5** is slower than rotation about the C–S bond of **1** (T_c for rotation in **1** = −136 °C and $\Delta\nu_{CH_3}$ = 11.0 Hz for the same sample).

The importance of π-bonding in CH_3COX (X = SH, OH, NH_2) is then expected to increase in the order X = SH < OH < NH_2.

Model Studies of the Biosynthesis of Non-Head-to-Tail Terpenes. Stereochemistry of the Head-to-Head Rearrangement [*J. Am. Chem. Soc.*, **99,** 3830 (1977)]. By C. DALE POULTER* and JOHN M. HUGHES, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

Page 3832: The positions of H_s and H_r should be reversed in structure 7-OH.

Book Reviews

Emission Spectroscopy. Edited by R. M. BARNES (University of Massachusetts). Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pa. 1976. xii + 543 pp. $35.00.

This book provides a complete overview and an in-depth look at more than a century of developments in emission spectrochemical analysis. Reproduced are 39 selected publications that document the landmark, breakthrough, and critical guiding pathways for change and maturity in the art of emission spectrochemical analysis. Editorial commentary is interposed throughout to provide additional insight for the reader and to cite pertinent references to original materials from which the reader can locate related publications. Topics covered include discharge sources, such as arcs, lasers, sparks and rf plasmas, photographic and photoelectric detector systems, gratings, spectrographs, and spectrometers.

The material is arranged in a semichronological manner, beginning with the pioneering efforts of Bunsen and Kirchhoff and continuing with a description of the history and literature of spectrochemical analysis. The contributions between 1860 and 1930 are grouped in Part I. Part II explores the growth of quantitative emission methods up to the present time. This section traces the developments in emulsion calibrations, spark sources, grating ruling and replication, multiplier phototubes, and techniques for solids, solutions, and microsamples. Semiquantitative and universal methods, advances in continuous current discharges, and matrix effects highlight Part III. Part IV deals with the time-resolution revolution. New spectroscopic sources, such as stabilized arc plasmas, high frequency, low pressure, or vacuum discharges and lasers, are emphasized in Part V. Finally, Part VI presents contemporary discoveries and discusses their impact on the future direction of emission spectroscopy.

The editor has succeeded admirably in his purpose which was to direct the curious and interested to events and publications that represent the critical stages in the growth of emission spectrochemical analysis. This fascinating book will be a valuable sourcebook for professionals and students alike.

John A. Dean, *University of Tennessee—Knoxville*

Cryochemistry. By M. MOSKOVITS (University of Toronto) and G. A. OZIN (University of Toronto). John Wiley & Sons, Inc., New York, N.Y. 1976. xi + 525 pp. $32.50.

As one feature, "Cryochemistry" describes some of the fascinating chemistry exclusive to the low-temperature environment and as its complementary feature, it reveals many of the technical pitfalls and solutions encountered in that arena of study. This work is not a comprehensive text, as the title might suggest, but rather various chapters contributed from seven different laboratories and centered around the unique and promising reactions of metal and nonmetal atomic vapors. The whole is rather loosely held together by two introductory chapters on technique. The potential problems of organization, duplication, and uneven coverage inherent in unreined multiauthored collections abound. Although two early chapters are entitled techniques, the first is rather sketchy apparently because discussions of this topic are actually spread throughout the remainder of the book. Nonetheless, this work possesses real strengths and is a significant contribution to the field. A large amount of very useful and practical information on low-temperature experiments is here collected in one place. This includes a unique in-depth description of devices for generating, reacting, trapping, and studying metal atoms. Also, much of the work (three chapters) reports techniques and reactions of metal atoms performed on a preparative scale with an eye to the future synthetic potential. The analytical scale atom chemistry (six chapters) is comprehensive in its coverage of reactions, and structure studies involving atoms of elements throughout the periodic table. A singular terminal chapter on the photochemistry of transition metal complexes gives limited but appropriate exposure to low-temperature photochemistry and rounds out the work.

This book should in general be useful on the academic and industrial stage to anyone contemplating or actively engaged in preparative or analytical research at low temperatures and is required reading to accompany studies (synthesis, catalysis, etc.) involving metal atoms.

James E. Gano, *University of Toledo*

Contact Catalysis. Volumes 1 and 2. Edited by Z. G. SZABO and D. KALLO (University of Budapest). Elsevier Scientific Publishing Co., Amsterdam and New York. 1976. 540 pp (Vol. 1), 480 pp (Vol. 2). $99.50 for two-volume set.

This comprehensive book covers most aspects of heterogeneous catalysis. It was prepared by a team of specialists under the auspices of the Catalysis Club of the Hungarian Academy of Sciences. The subject matter is divided into seven topical sections. After a theoretical presentation of the electronic structure of metals and semiconductors and adsorption, correlations of catalyst structure and activity are described. The kinetics of catalyzed reactions are detailed in the last part of Volume 1. The second volume is devoted to the preparation of catalysts and descriptions of various physical methods for surface characterization. Reactor design and other considerations in industrial applications of heterogeneous catalysis are covered in the final section. Many references are cited throughout the book, and complete author and subject indexes are included at the end of Volume 2.

This two-volume set represents one of the most detailed works on heterogeneous catalysis since Emmett's seven-volume series published in 1954–60. The theoretical discussions of most subjects are adequate, but some applied considerations of heterogeneous catalysis are covered scantily. Many other books have been published in recent years which provide more detailed treatments of the various topics in "Contact Catalysis". This book does, however, give an overview of heterogeneous catalysis, and should be a useful reference to scientists involved in catalytic research.

H. Heinemann, S. E. Voltz
Mobil Research and Development Corporation

Determination of Organic Structures by Physical Methods. Volume 6. Edited by F. C. NACHOD (Sterling-Winthrop Research Institute), J. J. ZUCKERMAN (Univ. of Oklahoma), and E. W. RANDALL (Queen Mary College). Academic Press, New York, N.Y. 1976. xiii + 453 pp. $47.00.

In a review of a book of this genre, it may be appropriate to proceed immediately to the "bottom line": this is not a volume which belongs in every chemist's personal library. It is, however, a book which deserves to be in every departmental or scientific library, and its acquisition in this context can be warmly recommended.

In this book, the editors have followed the precedent set by the earlier five volumes in this series, by collecting contributions written by practitioners of a variety of physical methods of structure determination of organic compounds (broadly interpreted) into a compendium of six chapters which are only loosely connected by a commonality of theme. The topics covered include "Amino Acid Sequencing by Mass Spectrometry", "Computerized Structure Retrieval and Interpretation of Mass Spectra", "Flash Photolysis and Structure", "^{29}Si Nuclear Magnetic Resonance," "The Nuclear Overhauser Effect", and "Molecular Structures by NMR in Liquid Crystals". Obviously, all of these chapters are unlikely to appeal to the top priority of interests of any single reader, but collectively they constitute a valuable reference source of information both with respect to fundamental principles as well as an entré to the current literature in the various cited fields. It will also be obvious from the chapter titles that the applicability of the individual topics to the problem of organic structure determination spans a rather wide range, being very immediate in the case of nuclear magnetic resonance techniques applied to liquid crystal systems, and somewhat less so in the discussion of flash photolysis and amino acid sequencing.

The indexing (both subject and author) appears to be satisfactory, and the text format related to labels, illustrations, and equation display makes this volume easy to read and utilize. The list of references cited by the individual authors are appropriate to the purposes of this volume. As stated above, the acquisition of this collection of chapters related to selected topics on the subject of organic structure determination can be said to be both appropriate and necessary for any complete reference library in chemistry. One may look forward to further additions to this useful series.

Rolfe H. Herber, *Rutgers, The State University of New Jersey*

Laser Spectroscopy of Atoms and Molecules. Edited by H. WALTHER (Universität München). Springer-Verlag, New York and Berlin. 1976. vii + 383 pp.

The invention of the laser over 15 years ago gave spectroscopists a tool of immeasurable value. For the first time, direct generation of monochromatic light with high power density was possible. In the intervening years, many areas of optical spectroscopy have blossomed as the result of the application of techniques new to optical spectroscopy and the availability of intense light sources. One result has been the discovery of many new energy levels and splittings and increased understanding of the electronic structure of atoms and molecules.

"Laser Spectroscopy" comprehensively reviews this rapidly developing field through six papers prepared by specialists. The first two chapters, "Atomic and Molecular Spectroscopy with Lasers" by H. Walther and "Infrared Spectroscopy with Tunable Lasers" by Hinkley, Nill, and Blum, give the reader a broad introduction to laser spectroscopy in the visible and infrared regions. These sections are straightforward and provide the nonspecialist with an introduction to methods and examples of specific problems. The following three chapters on double-resonance spectroscopy by Shimoda, Raman spectroscopy of gases by Cherlow and Porto, and linear and nonlinear phenomena in laser optical pumping by Decomps, Dumont, and Ducloy give a more specialized review of these important fields. The final chapter, "Laser Frequency Measurements, the Speed of Light, and the Meter" by Evenson and Petersen, considers the use of lasers as frequency and length standards.

Throughout this volume, the reader is offered tantalizing glimpses into the future of laser spectroscopy. The promise of more inventive techniques and exciting discoveries seems to be excellent. "Laser Spectroscopy" provides both neophyte and specialist with an excellent review of recent results and a catalyst for future work in this exciting field.

Thomas J. Herbert, *University of Miami*

Isolation and Identification of Drugs. Volume 2. Edited by E. G. C. CLARKE (University of London). The Pharmaceutical Press, London. 1975. xi + 388 pp. £ 13.50.

This volume presents analytical techniques and very extensive analytical data on some 250 drugs. Volume 2 is a supplement to Volume 1, so much so that it starts where Volume 1 left off, on page 871. The book consists of four parts. In Part 1 the authors present analytical techniques in detail. A good deal of this part reads like a laboratory manual with explicit directions for carrying out tests or drug determinations. Most of the chapters are supplements to those in Volume 1. However, there are new chapters on mass spectrometry and radioimmunoassay. The chapter on drug screening tests was completely rewritten.

Part 2 lists drugs in alphabetical order with structural formulas, physical and analytical data, toxicity, metabolism, and dosage presented below the drug names. Part 3 tabulates physical and analytical properties according to increasing numerical value. Each entry has a reference to Part 2. A considerable number of drug infrared spectra are given in Part 3. Part 4 alphabetically lists reagents used in Part 1, their concentrations, and instructions on their preparation where necessary. Also in Part 4 is a list of tests, and a bibliography for Volume 2. Volume 2 has a very extensive general index for both volumes.

This book was written especially for toxicologists who work with body fluids and post mortem materials. It should be very valuable to them and others interested in drug analysis of biological samples and pharmaceuticals.

Norman E. Hoffman, *Marquette University*

Structure of Liquids (Topics in Current Chemistry, Volume 60). Edited by P. SCHUSTER ET AL. Springer-Verlag, New York–Heidelberg–Berlin. 1975. 200 pp. $25.50.

"Another article on water? Why?" This is a question that was asked by Stuart A. Rice in the introduction to his review article. Fortunately for the reader, he found good reason to write the article, which will be extremely useful to all chemists interested in this important, complex liquid. This 60th volume of critical reviews on current status and future trends in chemical research contains two review articles: "Molecular Models for Solvation of Small Ions and Polar Molecules", by P. Schuster, W. Jakubetz, and W. Marius, and "Conjectures on the Structure of Amorphous Solid and Liquid Water", by S. A. Rice.

In their article, Schuster, Jakubetz, and Marius critically examine the recent developments in the theory of interactions between ions or polar molecules and the nearest solvent molecules in the solution. The authors first introduce theory of molecular interactions, concentrating both on electrostatic models and quantum mechanical calculations. Major emphasis is on theory but a brief discussion of experimental data on gas-phase solvation and ions in solution is also given. The extensive presentation of the results of various theoretical calculations arranged in very useful, informative tabulary form represents a very valuable aspect of the article. The bulk of the article deals with the theoretical work on ions in solution, but the difficult problem of solvations of polar molecules is also mentioned. The reader will certainly welcome the extensive list of references (256).

In the second article, Stuart A. Rice has done an outstanding job of presenting a lucid, critical discussion of the latest experimental and theoretical work dealing with the structure and properties of water. As is clear from the title, the author discusses amorphous solid water, mostly on the basis of his own recent work, and correlates its properties with those of liquid water. He shows convincingly the importance of the studies of amorphous solid water, which can be regarded as a model for liquid water. The results of x-ray, neutron diffraction, infrared, and Raman studies are discussed both for amorphous and liquid H_2O and D_2O. The reviewer appreciated the fact that within limited space the author gave a very clear picture of what type of information about water one can obtain from these various experiments. The presentation of the results of the various measurements established a sound starting point to test and/or propose new theoretical models of amorphous and liquid water. The author reviews briefly the relevant features of both continuous and mixture models and the molecular dynamics and Monte Carlo simulations. All this information leads to a conjecture concerning the structure of the low- and high-temperature amorphous solid water and liquid water. A discussion of a possible experimental test for his continuous random network models of amorphous water concludes this review article.

In summary, this monograph will be valuable not only to experts in the field but to all chemists who want to familiarize themselves with the latest work dealing with water and aqueous solutions. Anyone interested in water must take time to read this book.

Jiri Jonas, *University of Illinois—Urbana*

Terpenoids and Steroids. Volume 6. Senior Reporter: K. H. OVERTON. The Chemical Society, London. 1976. x + 363 pp. £20.50.

In publishing the Specialist Periodical Reports, the Chemical Society has provided the scientific community with an invaluable aid to keeping abreast of a burgeoning literature. The sixth volume of "Terpenoids and Steroids" to appear since 1971 covers the literature from September 1974 to August 1975. The topics are divided into two parts; Part I, dealing with all terpenoids exclusive of steroids and including a chapter on biosynthesis, entails 1366 references whereas Part II presents a discussion of steroid chemistry (480 references).

The terse but comprehensive coverage of each class of terpenoid is presented in terms of structure, stereochemistry, physical methods, reactions, and synthesis. The absence of a subject index is largely compensated by extensive use of schemes and structures thereby facilitating rapid visual information retrieval, and by a logical and systematic organization. Students and researchers concerned even peripherally with the chemistry of the terpenoids are indebted to the 11 reporters for the excellence and currency of their respective contributions.

P. J. Kocienski, *Leeds University*

Spectroscopy of the Excited State. Edited by B. DI BARTOLO (Boston College). Plenum Press, New York and London. 1976. xiv + 416 pp. $32.50.

The NATO Advanced Study Institute on "The Spectroscopy of the Excited State" was held at Erice, Italy, June 9–24, 1975. This volume contains the principal lectures presented there, and was published as Volume 12 in the NATO Advanced Study Institutes Series. Introductory lectures were given on the "Interaction of Radiation with Atoms and Molecules" by the editor, B. Di Bartolo, and on "Introduction to Molecular Spectroscopy" by D. A. Ramsay. These were followed by ten lectures on current research, namely "Laser Excitation of Optical Spectra" by D. A. Ramsay, "Techniques of Flash Photolysis" by S. Claesson, "Some Fast Reactions in Gases Studied by Flash Photolysis and Kinetic Spectroscopy," by R. G. W. Norrish, "Electronic and Vibrational Energy Transfer" and "The Chemical Production of Excited Species" by B. A. Thrush, "Two-Photon Spectroscopy in the Gas Phase" and "Lifetime Spectroscopy" by E. W. Schlag, "The Study of Electronic Spectra in Crystalline Solid Solutions" by D. S. McClure, "Core Excitation and Electron Correlation in Crystals" by S. Sugano, and "Molecular Excitons in Small Aggregates" by M. Kasha. In addition this volume contains abstracts of 21 shorter presentations and a brief subject index.

As the NATO Advanced Study Institutes serve both as "courses" and as research conferences, this volume is valuable both as an advanced textbook and as a presentation of current spectroscopic methods and results. Thus it should be of particular interest to those planning new research programs in spectroscopy.

Lawrence L. Lohr, Jr., *University of Michigan*

New Applications of Organometallic Reagents in Organic Synthesis. Proceedings of a Symposium at the American Chemical Society National Meeting, New York, 1976. Edited by D. SEYFERTH. Elsevier Scientific Publishing Co., New York, N.Y. 1976. 488 pp. $44.75.

This text has been written by practitioners of the ever-growing organometallic chemistry. Numerous examples of elegant chemical transformations of organic molecules have been put together under the following titles: Organolithium Compounds in Organic Synthesis, Recent Developments (D. Seebach and K.-H. Geiss); Organoboron and Organoaluminum Compounds as Unique Nucleophiles in Organic Synthesis (E.-I. Negishi); Organosilicon Compounds in Organic Synthesis (P. F. Hudrlik); The Applications of Organotin Reagents in Organic Synthesis, Recent Advances (M. Pereyre and J.-C. Pommier); Organocopper Reagents in Organic Synthesis (J. F. Normant); Organomercurials as Reagents and Intermediates in Organic Synthesis (R. C. Larock); Transition Metal Carbonyls as Reagents for Organic Synthesis (H. Alper); Application of π-Allyl Transition Metal Complexes In Organic Synthesis (L. S. Hegedus); Arenemetal Complexes in Organic Synthesis (M. F. Semmelhack); α-Anions of Metal Carbene Complexes in Organic Synthesis (C. P. Casey); The Olefin Metathesis Reaction (R. H. Grubbs); Transition Metal Hydride Reagents for Organic Synthesis (J. Schwartz).

In general, except for the detailed kinetic interpretation advanced by Grubbs with regard to the olefin methathesis reaction, this text reviews the fast expanding areas of organometallic chemistry in a format that should be attractive to both synthetic and physical organic chemist. In particular, it is refreshing to note that the chemistry described throughout is well balanced with concepts of synthetic methodology and mechanistic interpretations of various phenomena heretofore only referred to as "black magic". Furthermore, authors in this text have admirably explained lucidly the role of metals in these inorganic–organic reactions. This is a very welcome and healthy trend.

In as much as this is perhaps one of the best texts of its kind in the market, I must comment about the exorbitant amount of money for the sometimes poorly typed text. It is rather disturbing to have to pay for text, portions of which are filled with untidy editing (pp 28, 38, and 51). All in all, except for the price, this is an excellent book.

King Way Ma, *Dow Chemical Company*